MIT Energy Initiative
Cambridge MA

New Vistas in Electrochemical Energy Storage

Sept 7, 2016

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Senior Canada Research Chair

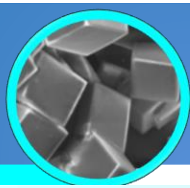
***E**lectrochemical **E**nergy **M**aterials **L**aboratory*

BASF International Scientific Network for Electrochemistry and Batteries

Joint Center for Energy Storage Research

DOE, USA

Thanks to:



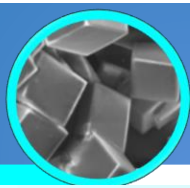
C. Xia, R. Black, R. Fernandes, D. Kundu, X. Liang, X. Sun, P. Bonnick, V. Duffort, B. Adams

BASF The Chemical Company

NSERC CRSNG

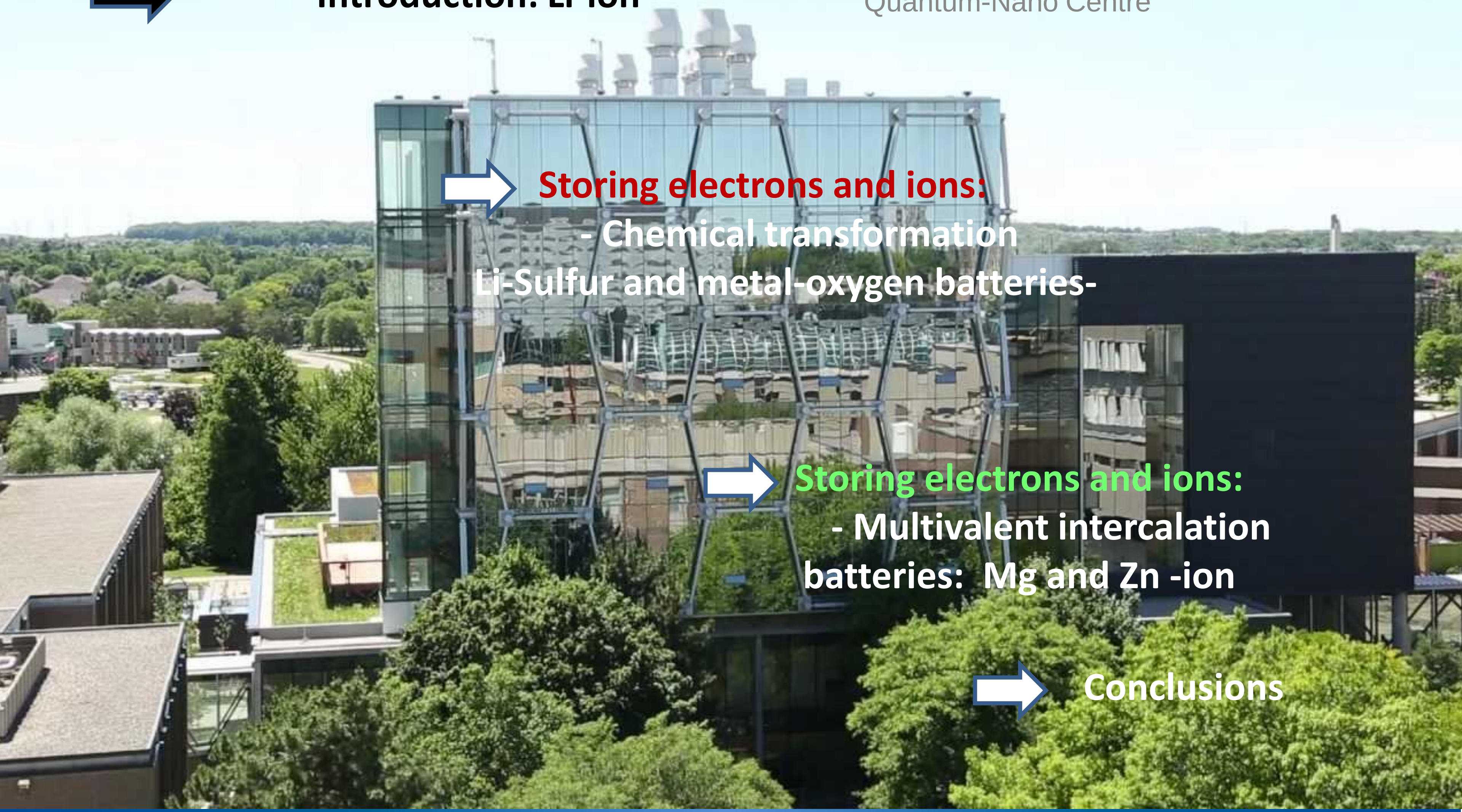
JCESR

Agenda :



Introduction: Li-ion

Waterloo Institute for Nanotechnology and the Quantum-Nano Centre



Storing electrons and ions:
- Chemical transformation
Li-Sulfur and metal-oxygen batteries-

Storing electrons and ions:
- Multivalent intercalation
batteries: Mg and Zn -ion

Conclusions

Global Energy Assessment: Cambridge Univ Press, 2012

GEA – the first global and interdisciplinary assessment of energy challenges and solutions – identifies 41 pathways to provide sustainable energy for the world by 2050

"Integrated energy storage is an area where technology lags and needs intense development if systems with optimum overall efficiency gains are to be attained"

Energy Storage: A Challenge of the 21st Century

New electrochemical energy storage chemistry needed

Exploit renewable energy resources	Power the world: big computing, small devices	Enable low cost, high range electric vehicles

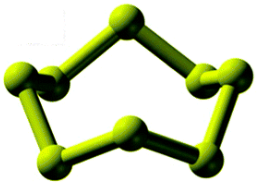
Different energy needs

Different materials

Different cost point

Wind / Solar	Smart energy delivery	Electric (+ solar): Kiira Motors
MWh	**Wh - MWh**	**kWh**

Chemical energy to electrical energy and work (downhill, discharge)



Chemicals

Batteries

Electricity

Electrical energy back to chemical energy (uphill, charge)

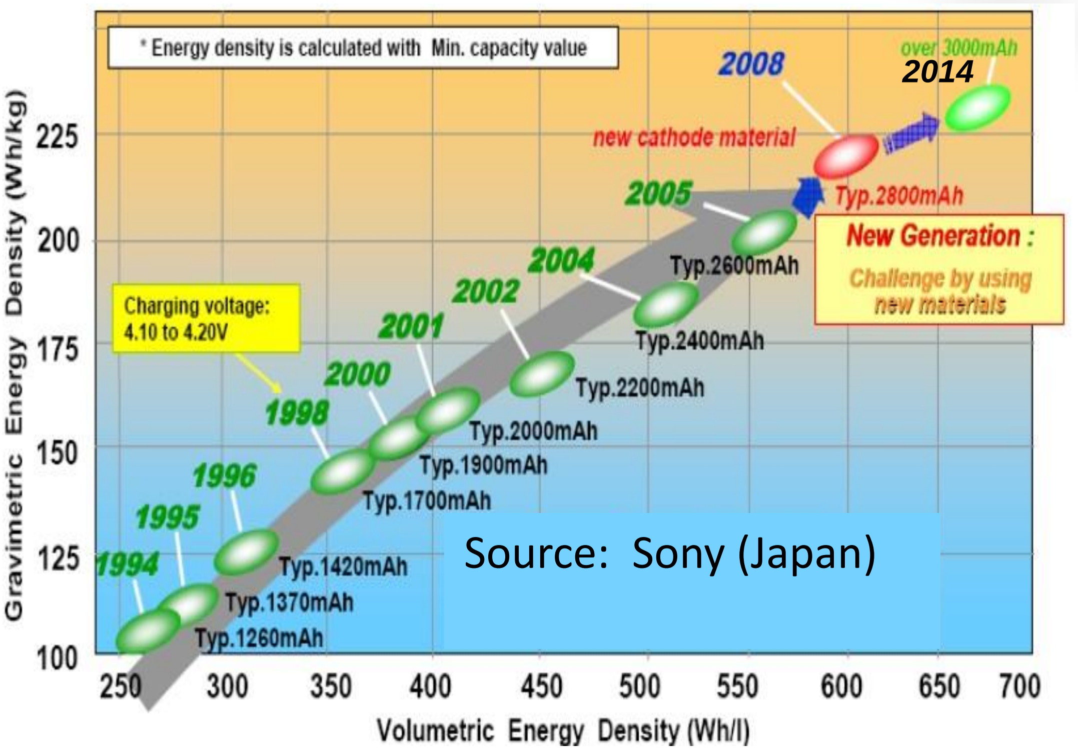
Progress in Li-ion technology: driven by portable devices

Capacity:
Electrons stored per mass (mAh/g) or volume (mAh/L)

⇩

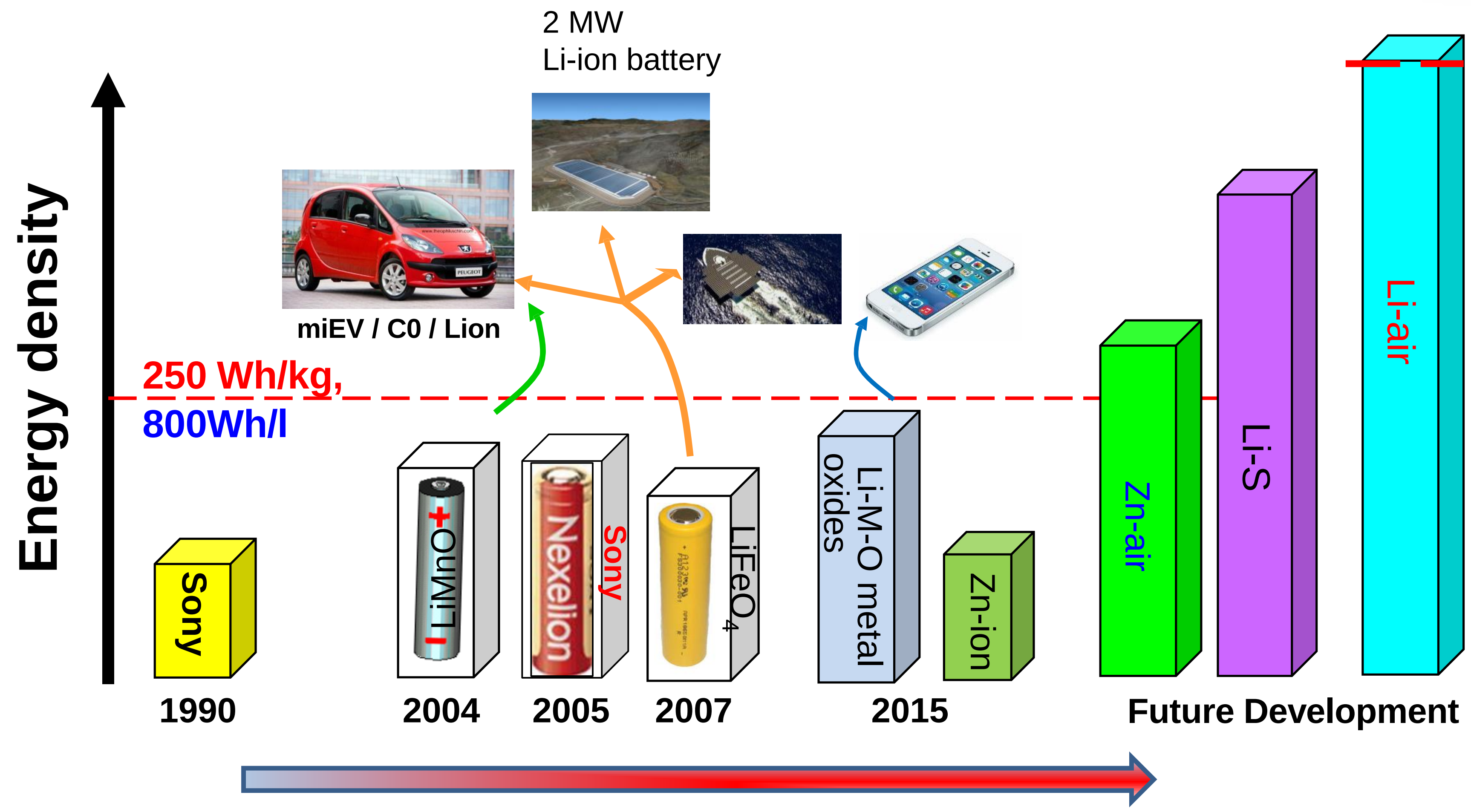
Light weight/dense

Capacity * Voltage = Energy density Wh/kg or Wh/L

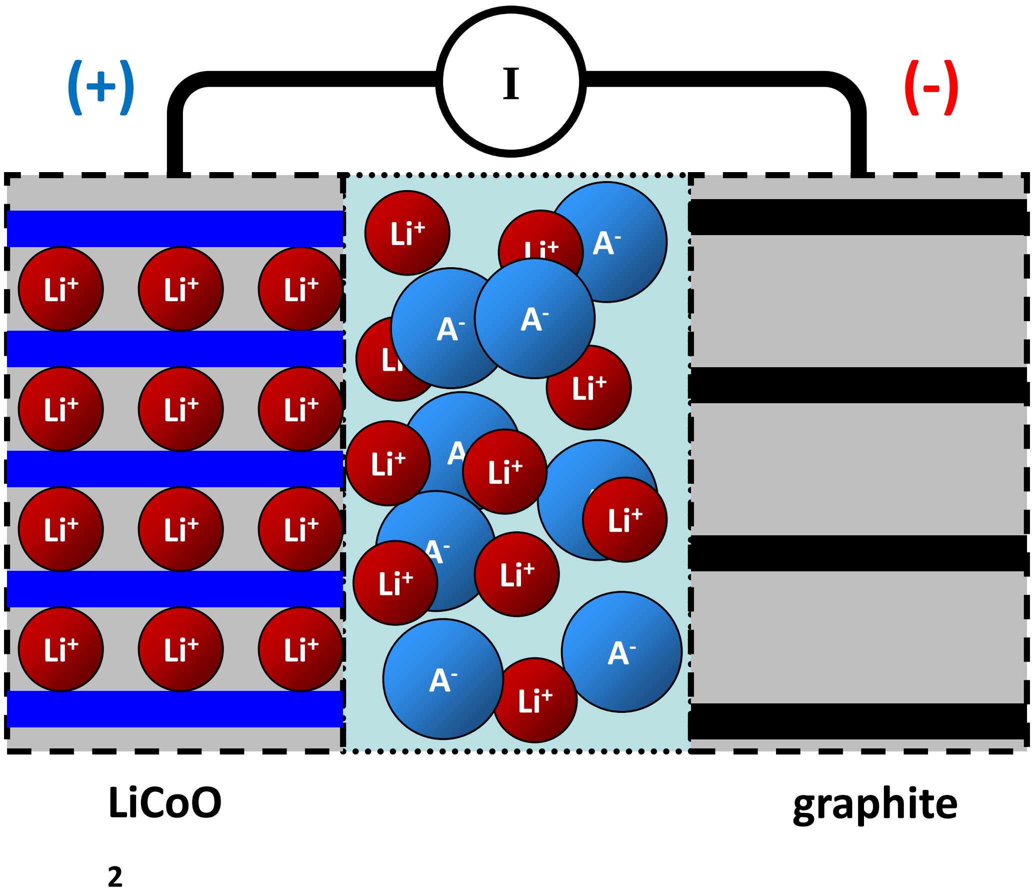


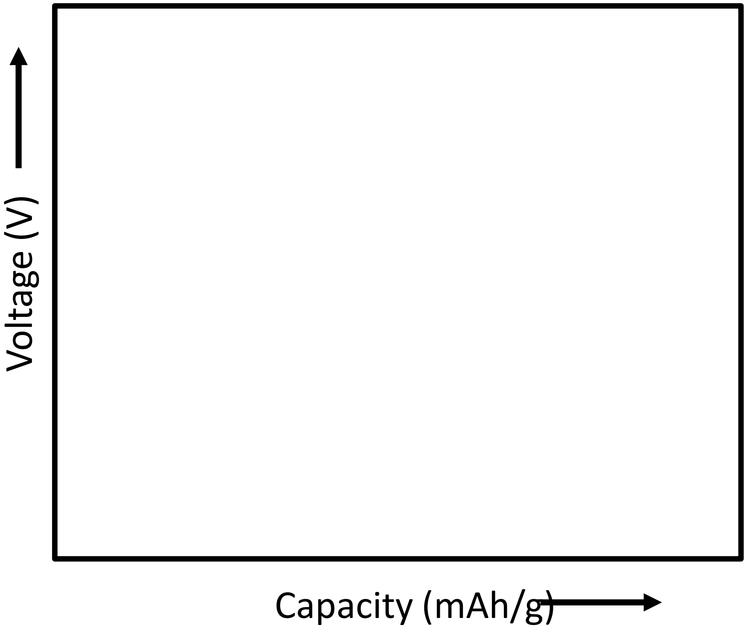
Increase in energy density by year for 18650 cells
Limit ~ 280 Wh/kg based on “intercalation” chemistry
Problems: cost, safety

Energy storage perspective: 2x in ED, -2x in cost

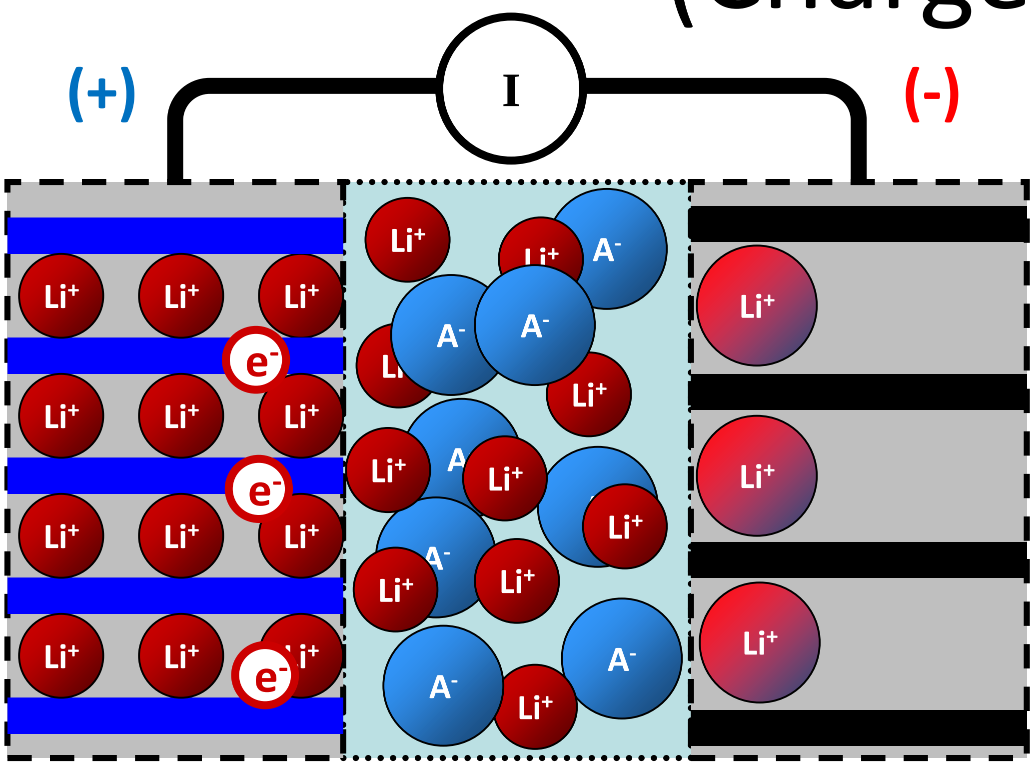


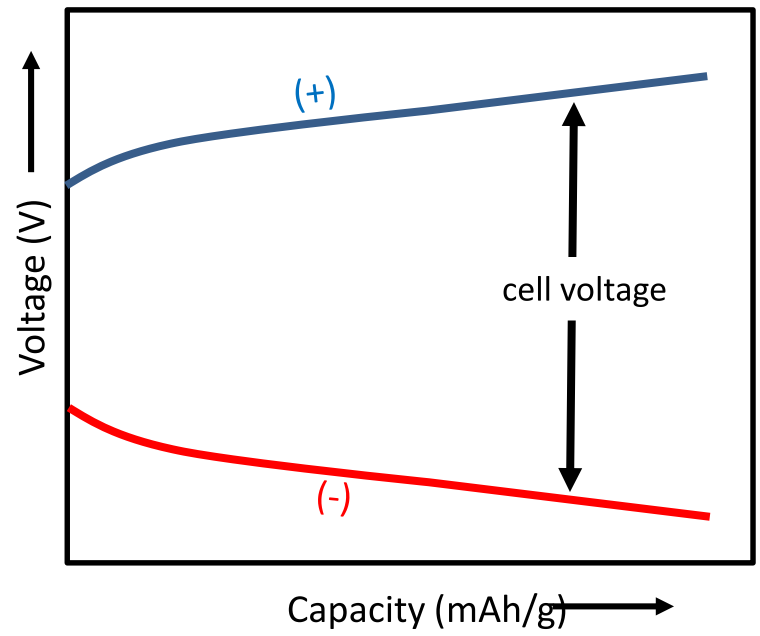
Li-Ion Cell Operation





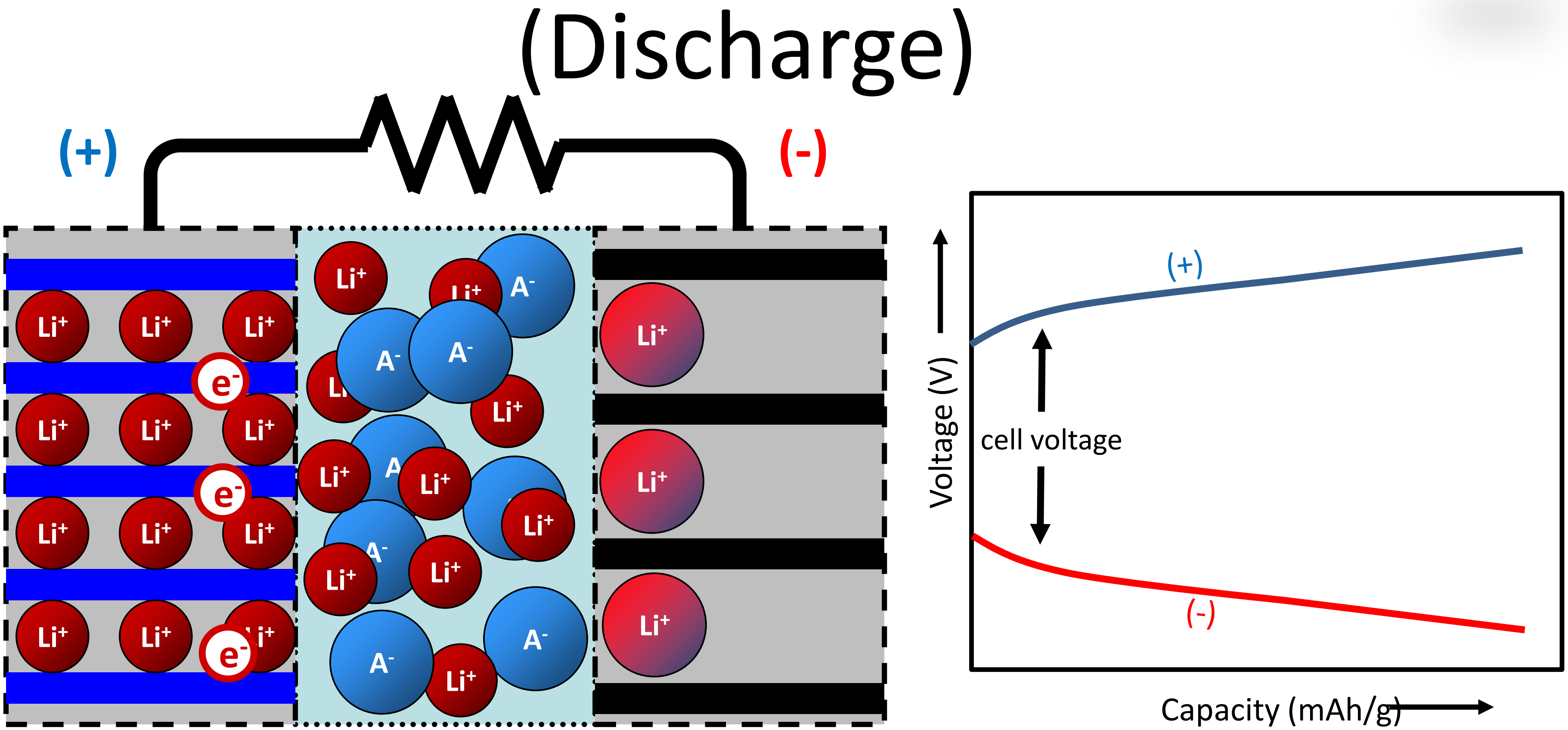
(Charge)





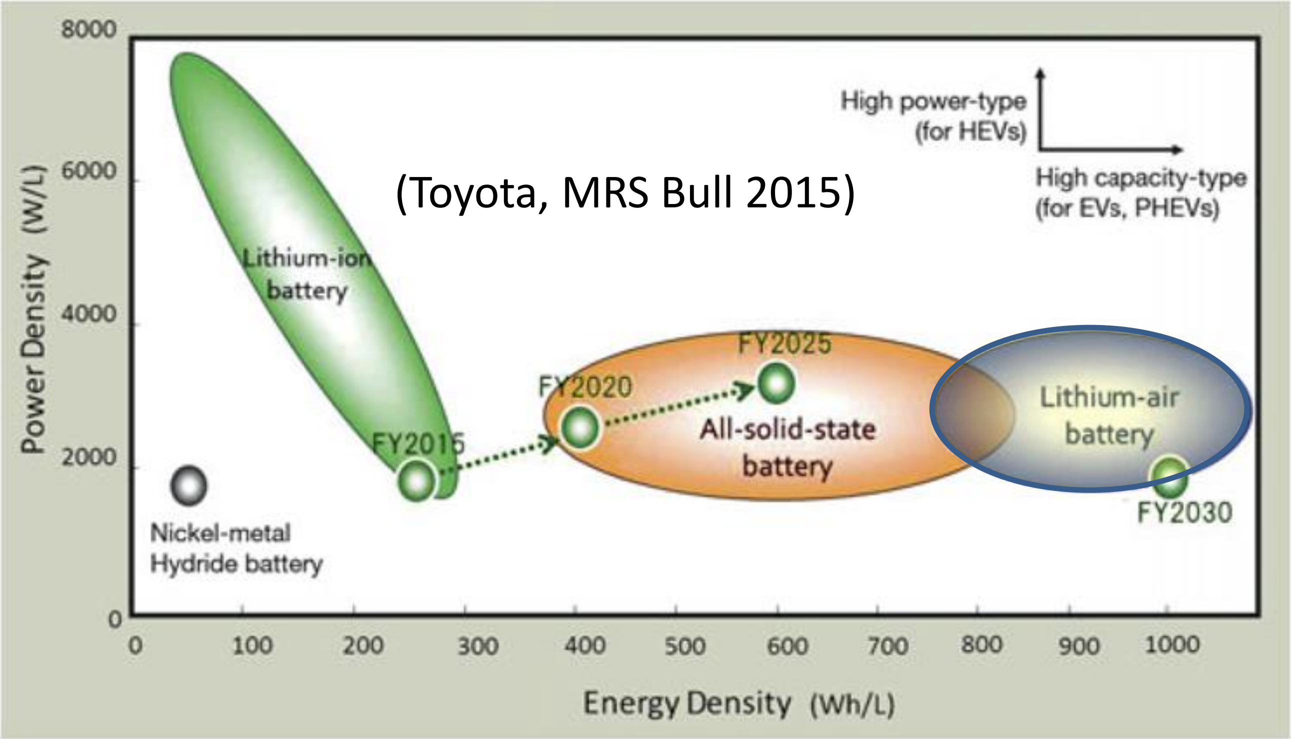
$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$ $xLi^+ + xe^- + C \rightarrow Li_xC$

Li-Ion Cell Operation



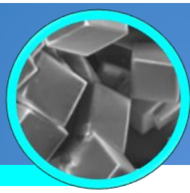
$Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$ $Li_xC \rightarrow xLi^+ + xe^- + C$

Vehicular energy storage: looking to the far future



All-solid-state batteries (Li, Na, Li-S, etc) have in common with Lithium-air the requirement of strict control of electrochemical interfaces

Ion intercalation vs chemical transformations



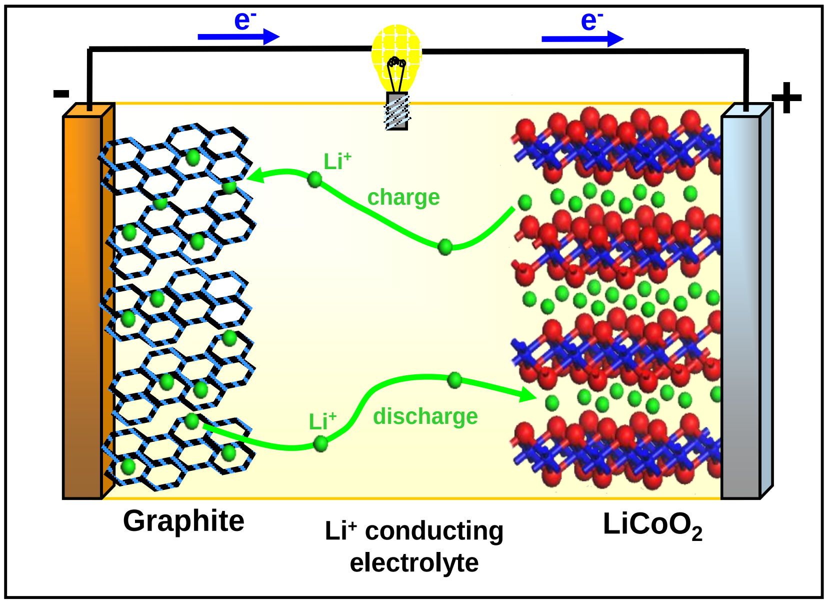
Transition metal oxides: good e^- transport

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

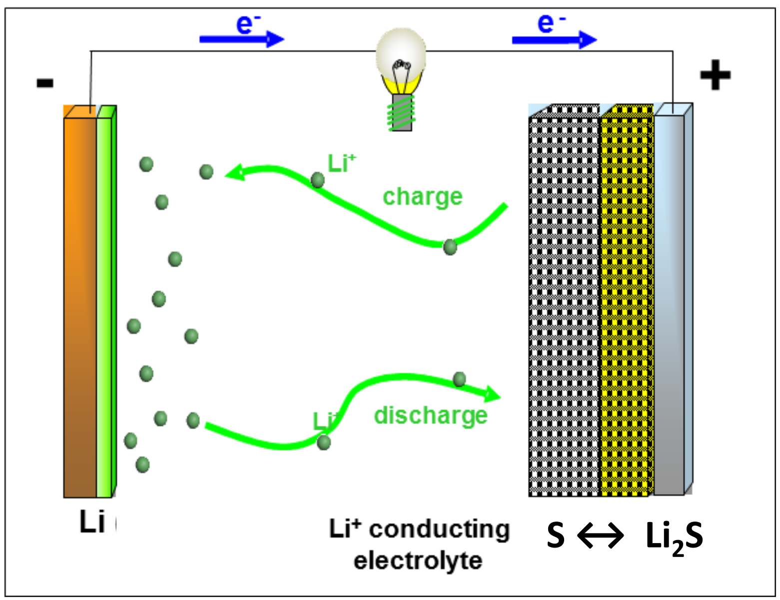
Chalcogens: light weight

16	O
32	S
3	Se
52	Te
84	Po

Intercalation cell



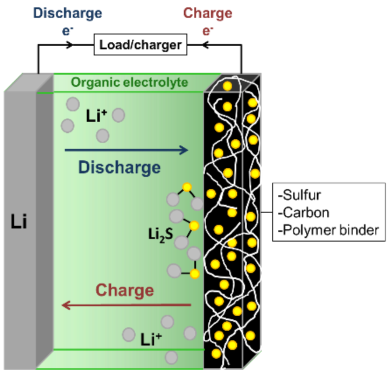
Chemical Transformation cell



Step change → **Dissolution-precipitation**

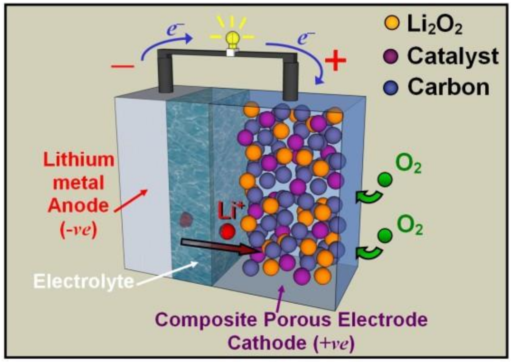
Lithium-chalcogenide (O_2, Sulfur) batteries: similar

Li-Sulfur



Earth abundant inexpensive

Li-Oxygen



$2Li^+ + 2e^- + S \leftrightarrows Li_2S$ (E°= 2.27 V)
Energy density = 2500 Wh/kg

$2Li^+ + 2e^- + O_2 \leftrightarrows Li_2O_2$ (E°= 2.96V)
Energy density = 3500 Wh/kg

Factor of 7

$0{,}7Li^+ + 0.7e^- + Li_{07}MO_2 \leftrightarrows LiMO_2$
Energy density = 220 Wh/kg

Factor of 3.5

≈ 350 Wh/kg

650 Wh/kg possible?

≈ 200 Wh/kg

x 3

≈ 1000 Wh/kg

..but limited cycling

Redox transform electrochemical systems

$Li^+ + e^- + 2\ Li_{0.5}CoO_2 \rightarrow 2\ LiCoO_2$

MW/e⁻ = 196

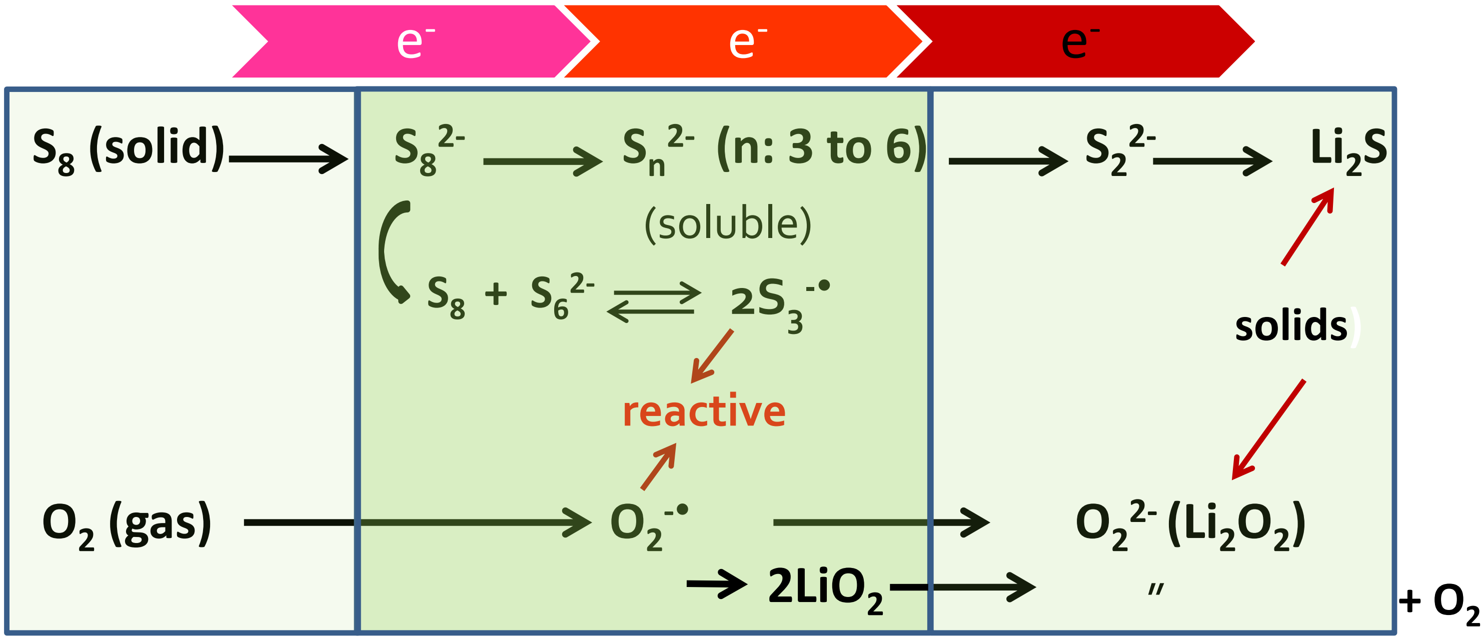
$S_2 + 2\ Li^+/e^- \leftrightarrow Li_2S$

MW/e⁻ = 23

$O_2 + 2\ Li^+/e^- \leftrightarrow Li_2O_2$

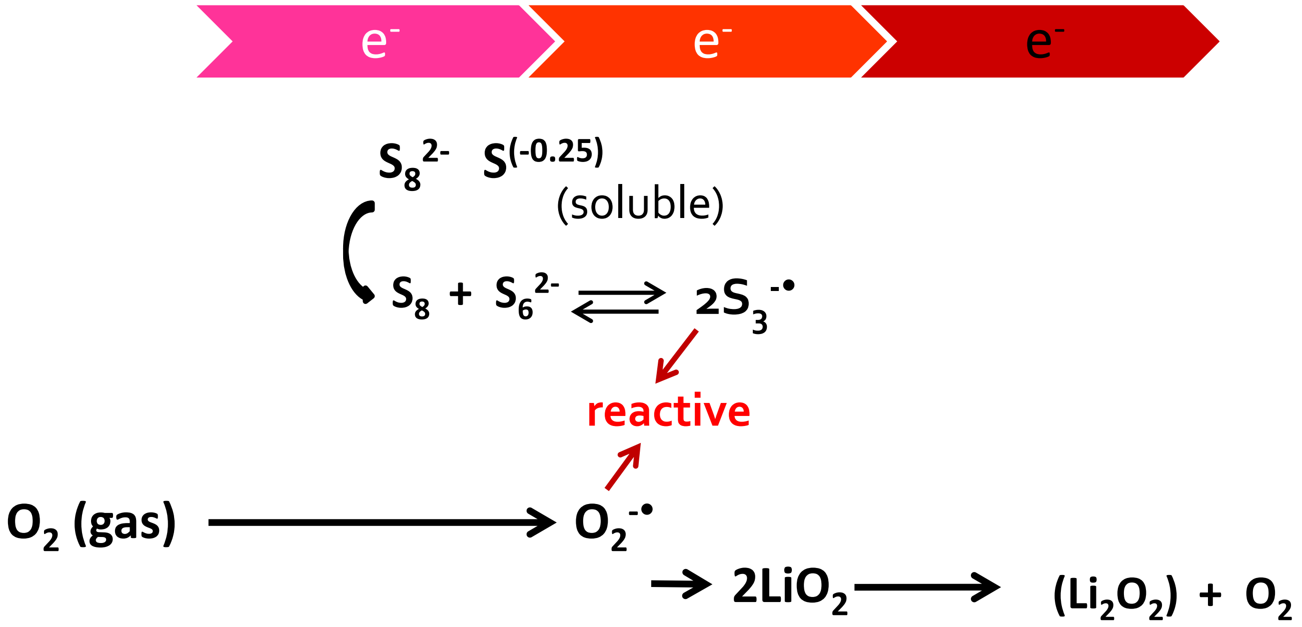
MW/e⁻ = 23

- **Dissolution-crystallization and disproportionation chemistry**



Redox transform electrochemical systems

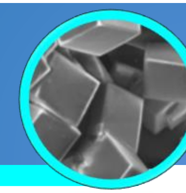
- **Dissolution-crystallization and disproportionation chemistry**



- **Prone to disproportionation reactions**
- **Intermediates in the electrochemical reactions very problematic**

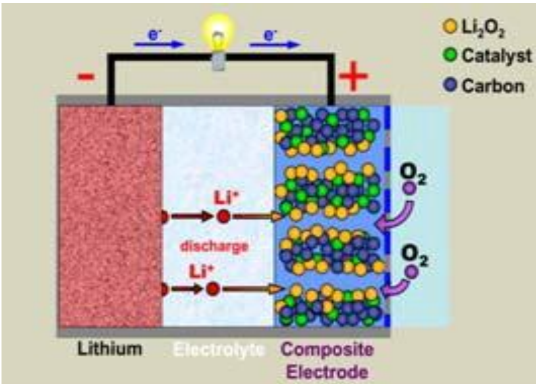
Reactive radicals

➔ **Aging**



Li-O_2 batteries: a lot of hype, a lot of challenges

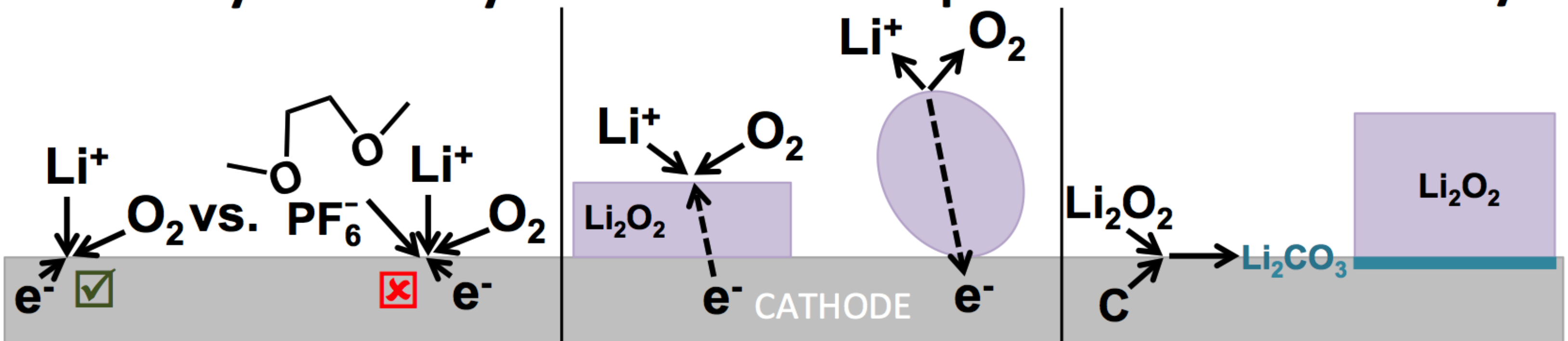
$$O_2 + 2\,Li^+/e^- \leftrightarrow 2\,LiO_2 \rightarrow Li_2O_2 + O_2$$



Positive Electrode

- *minimal* overpotential for oxygen reduction
- reactivity of host electrode with Li_2O_2
  - → nanoporous, stable conductive host
- Overcome large overpotential on charge

Electrolyte Stability | **Electron Transport** | **Cathode Stability**

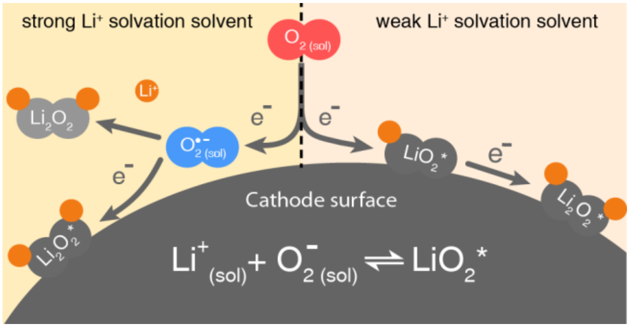


Review of Li-O_2: D. Aurbach, B. McCloskey, L.F. Nazar, P. Bruce* *Nature Energy (in press, 2016)*

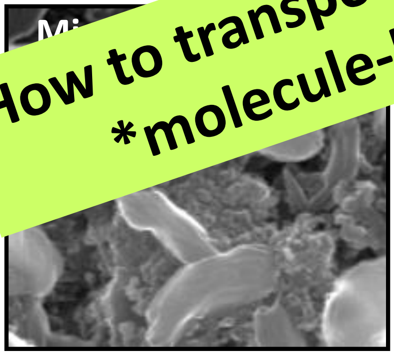
A long term prospect

But….steps forward in understanding

Discharge: $Li^+/e^- + O_2 \rightarrow LiO_2 \rightarrow$



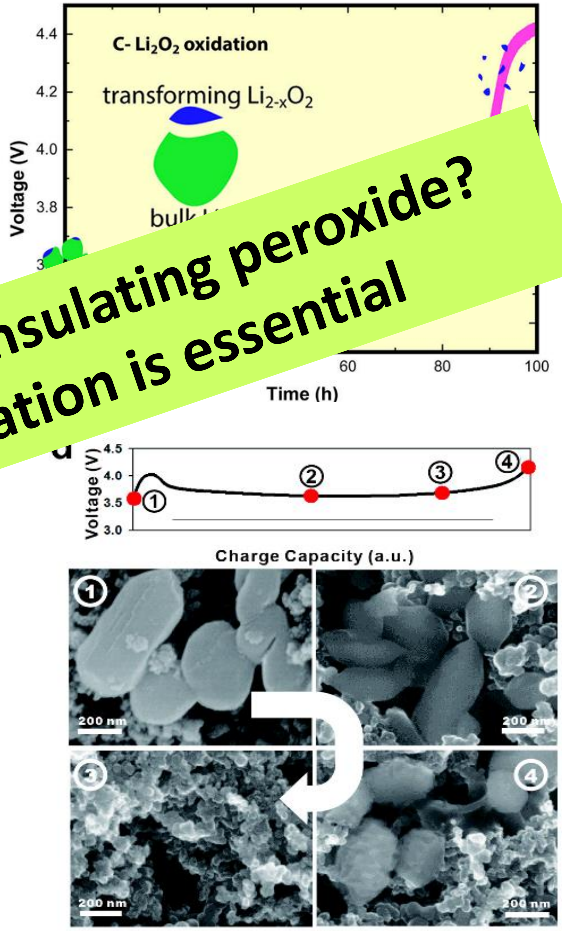
Superoxide formed on surface: dissolution competes with 2nd reduction : depend... current density and solvation



L. Nazar et al., JACS 2013; *EES (2013); Y. Shao-Horn, JPCL, 2013*

Favour large aggregates via $O_2^{-\bullet}$ transport

Charge: $Li_2O_2 \rightarrow Li_{2-x}O_2 + x\ Li^+/e^-$



$Li_{2-x}O_2 \rightarrow O_2 + x\ Li^+ + x\ e^-$

M. Wagemaker, Nazar et al., *JACS (2015), JPCL 2016*

How to transport electrons to/from insulating peroxide?
***molecule-based solution mediation is essential**

Inherent solution mediation in Na-oxygen cells

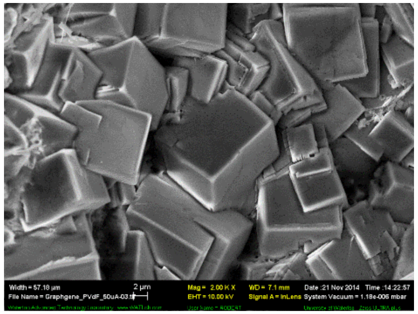
LETTERS
PUBLISHED ONLINE: 2 DECEMBER 2012 | DOI: 10.1038/NMAT3486
nature materials

A rechargeable room-temperature sodium superoxide (NaO_2) battery

Pascal Hartmann[1], Conrad L. Bender[1], Miloš Vračar[1†], Anna Katharina Dürr[2], Arnd Garsuch[2], Jürgen Janek[1*] and Philipp Adelhelm[1*]

Theor: 1600 Wh/kg

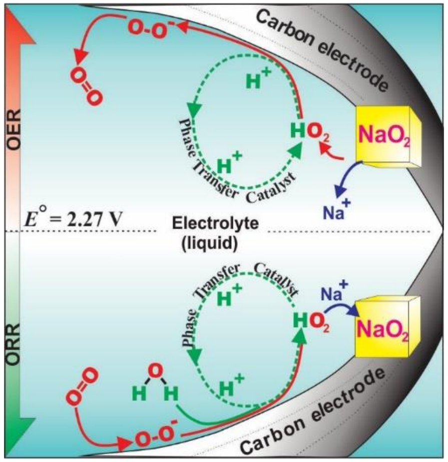
$$O_2 + Na^+/e^- \leftrightarrow NaO_2$$



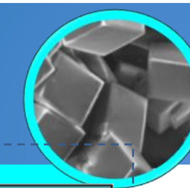
ARTICLES
PUBLISHED ONLINE: 18 MAY 2015 | DOI: 10.1038/NCHEM.2260
nature chemistry

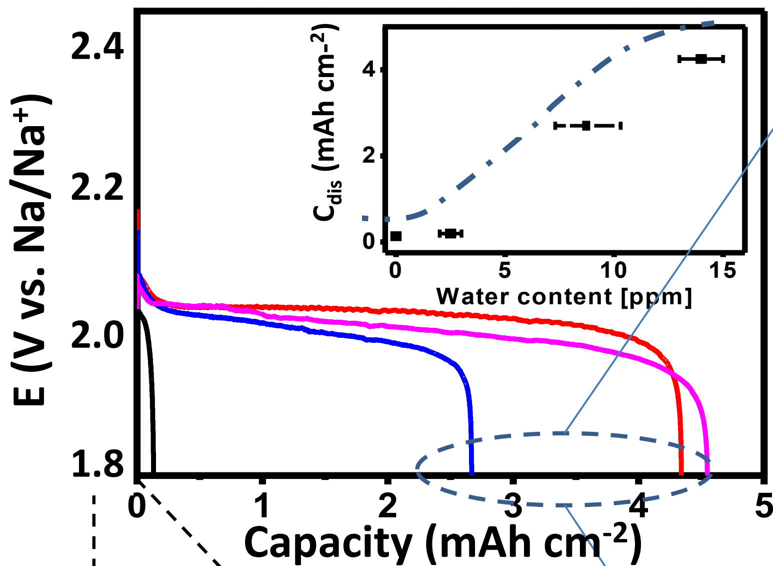
The critical role of phase-transfer catalysis in aprotic sodium oxygen batteries

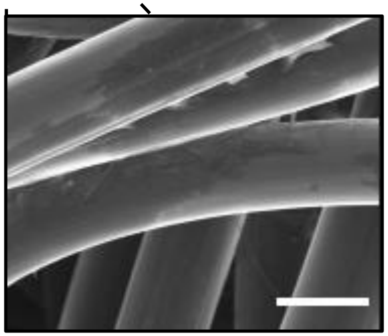
Chun Xia, Robert Black†, Russel Fernandes†, Brian Adams and Linda F. Nazar*



Na-O_2 Battery: phase transfer catalysis, high capacity





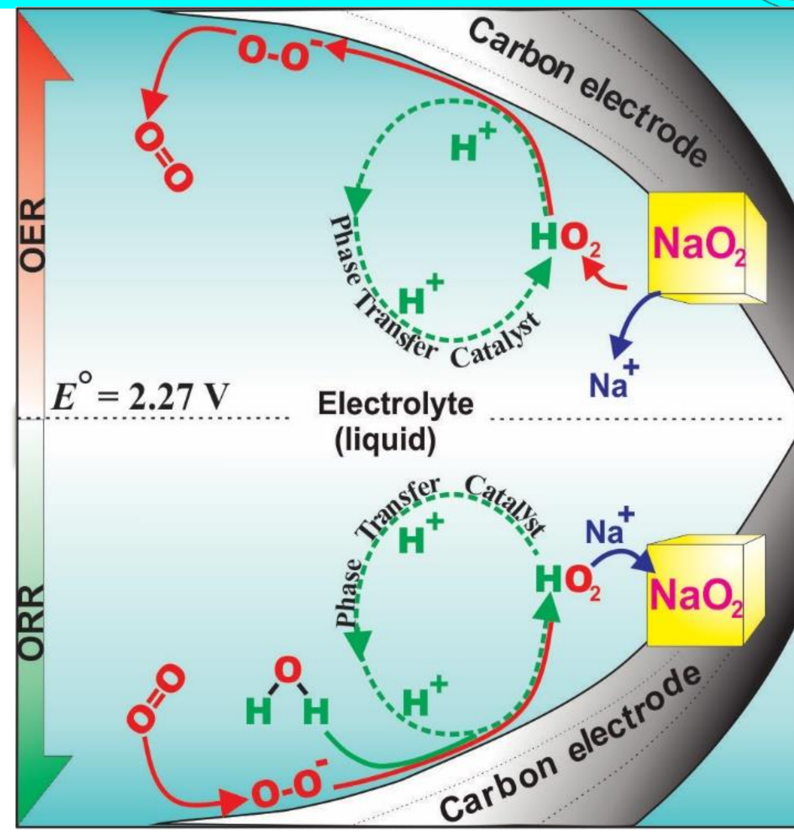


0 ppm H_2O

Quasi-amorphous NaO_2 films

Negligible capacity

Surface Mechanism



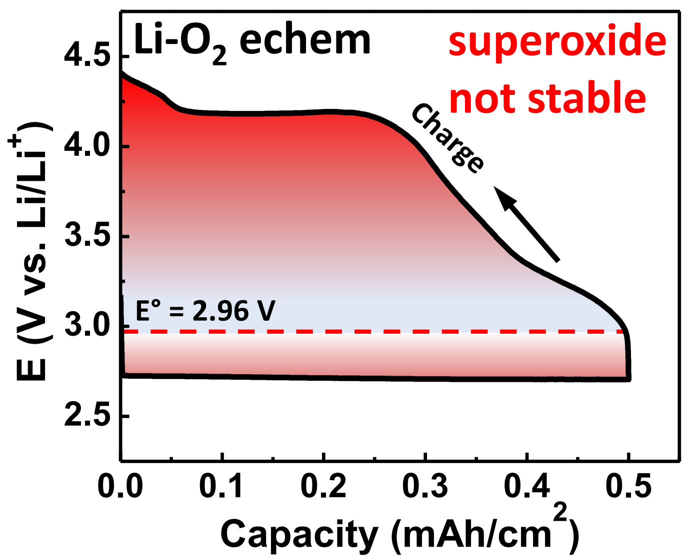
$HA + O_2{\bullet}^- \leftrightharpoons HO_2 + A^-$

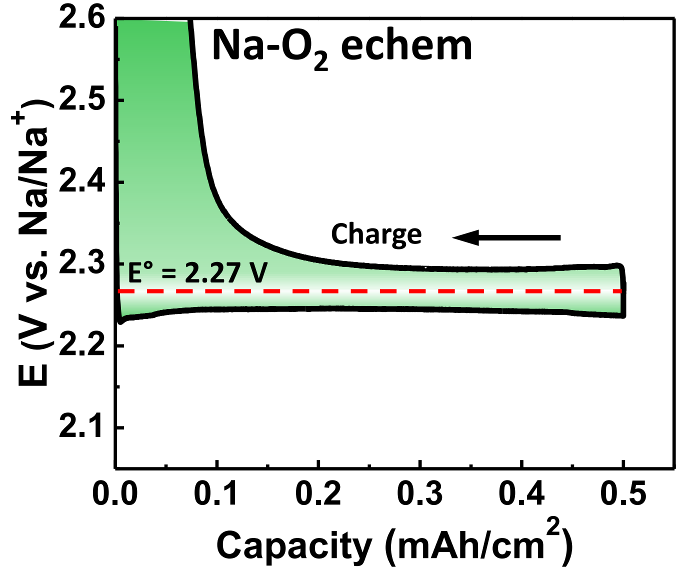
$HO_2 + Na^+ \rightarrow NaO_2 + H^+$

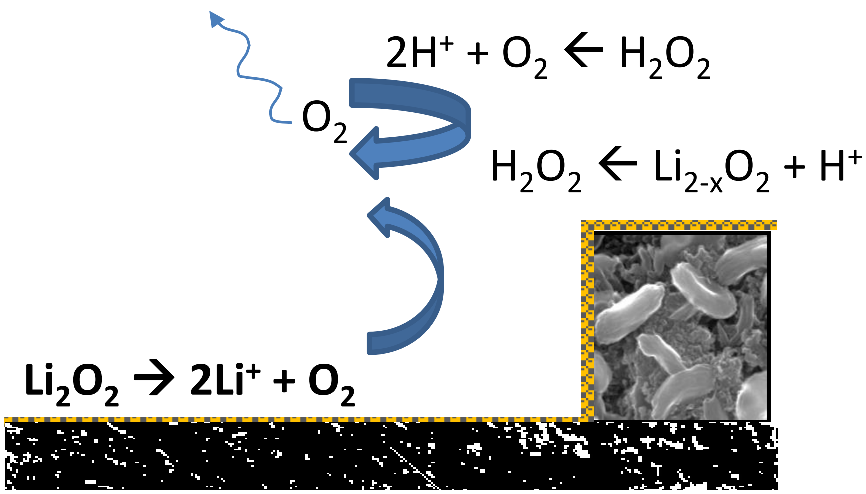
reverse on charge

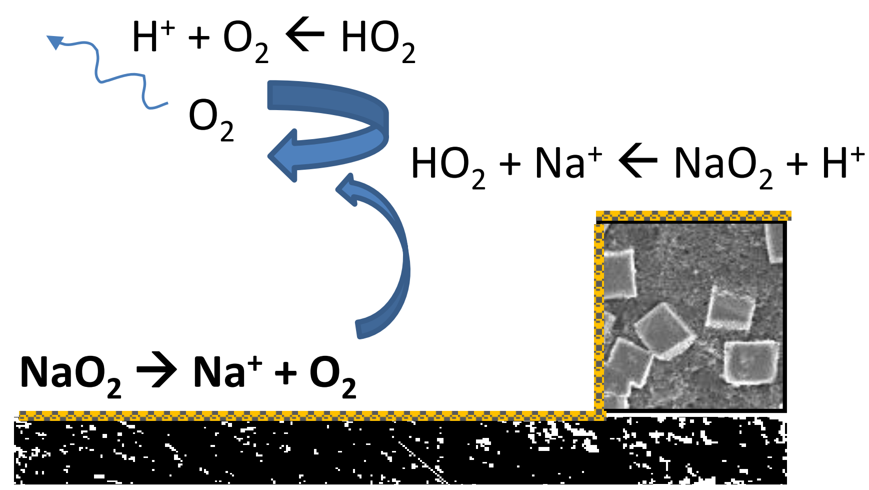
Xia, Nazar et al. *Nature Chemistry* **2015**, 7, 496–501

Phase transfer catalysis not possible for Li-O_2

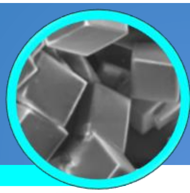




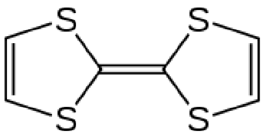




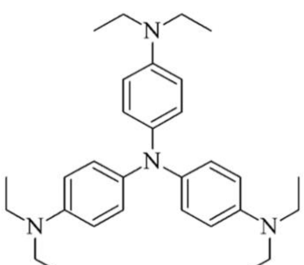
Redox Mediators – THE solution on charge (& discharge)



Soluble molecules in the electrolyte oxidized at a potential slightly above the equilibrium potential of Li_2O_2.

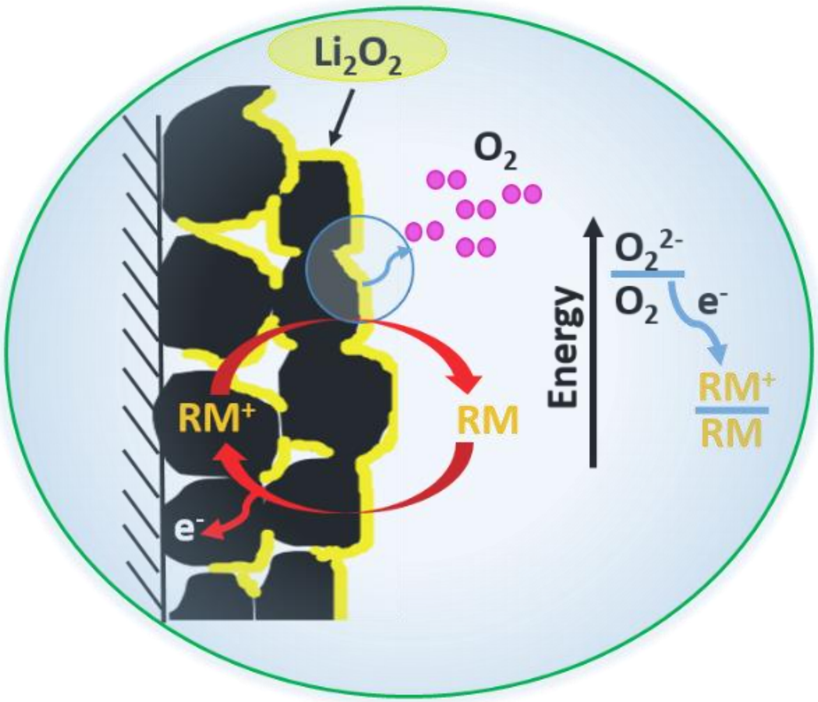


TTF- TTF^+/3.5-3.7V
P.G. Bruce *et al*,
Nature Chemistry, 2014

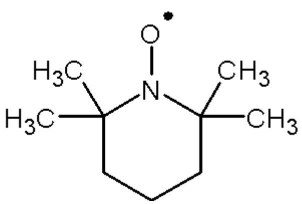


TDPA

$TDPA - TDPA^+ - TDPA^{2+}$
3.1/3.5 V
L. Nazar *et al*,
ACS Central Sci, 2015



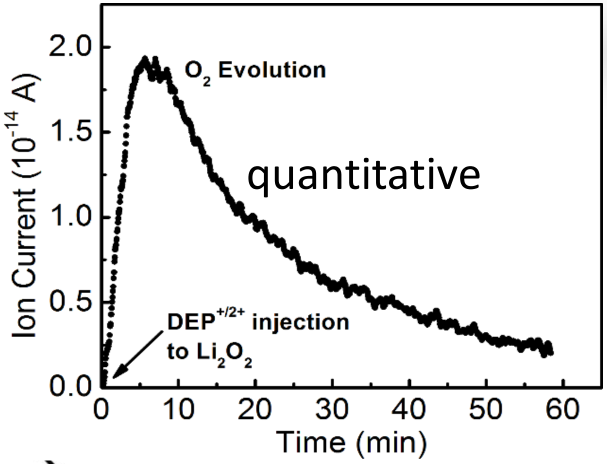
Br^-/Br_2
D. Aurbach *et al*,
Angew Chemie, 2016

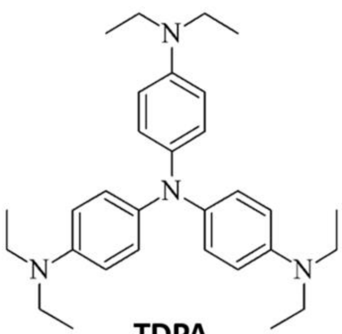


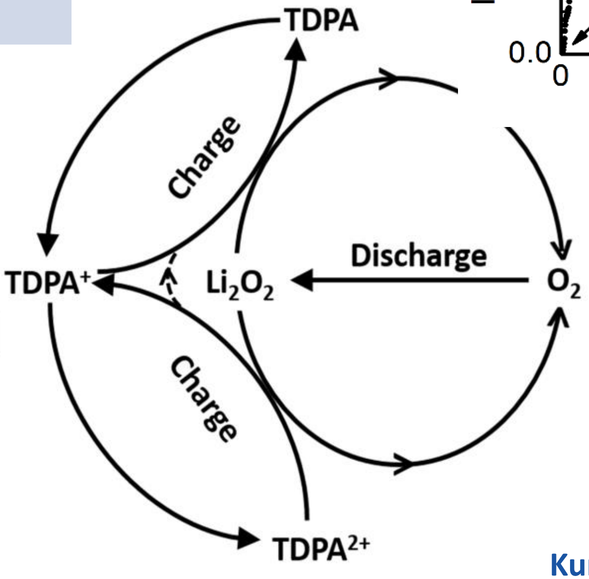
$TEMPO- TEMPO^+$
3.8V
J. Janek *et al*, *JACS*, 2015

A Dual Step Redox Mediator for Li-O_2 Cell

	RM/RM^+	RM/RM^{2+}
TTF	3.5 V	3.7 V
TEMPO	3.8 V	
TDPA	3.1 V	3.5 V







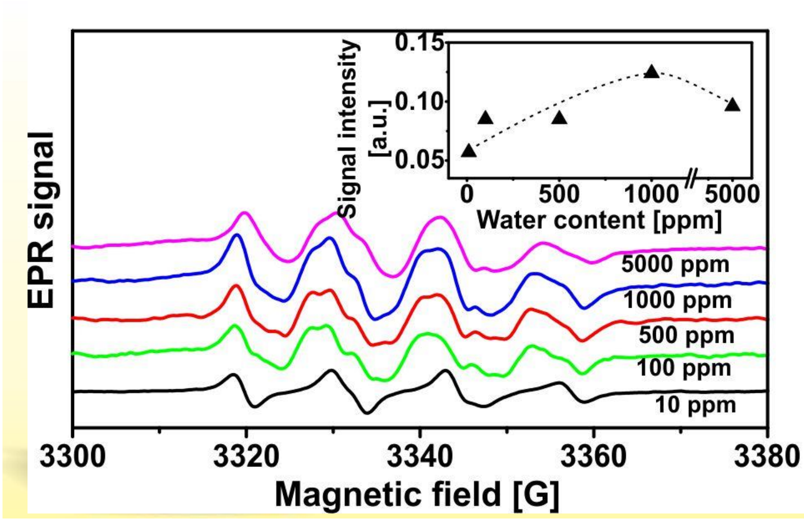
Kundu, Nazar et al.,
ACS Central Science, 2015

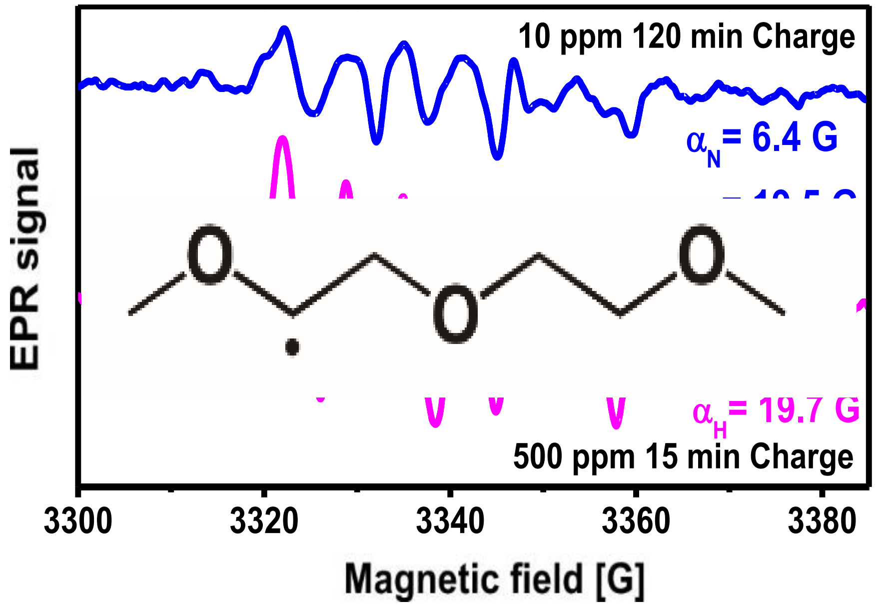
Requires that the negative Li electrode be passivated

Detrimental reactivity of HO_2 with glyme electrolyte

Charge

"Operando" ESR studies show HO_2 generates glyme radicals ➔ electrolyte decomposition products





Find electrolytes stable to radical (HO_2) hydrogen abstraction

C. Xia, L. Nazar, J. Baugh et al., *J. Am Chem. Soc (2016)*

Down the Periodic Table

The Li-S Battery and the Redox Shuttle

$2Li + S \leftarrow Li_2S_x \rightarrow Li_2S$

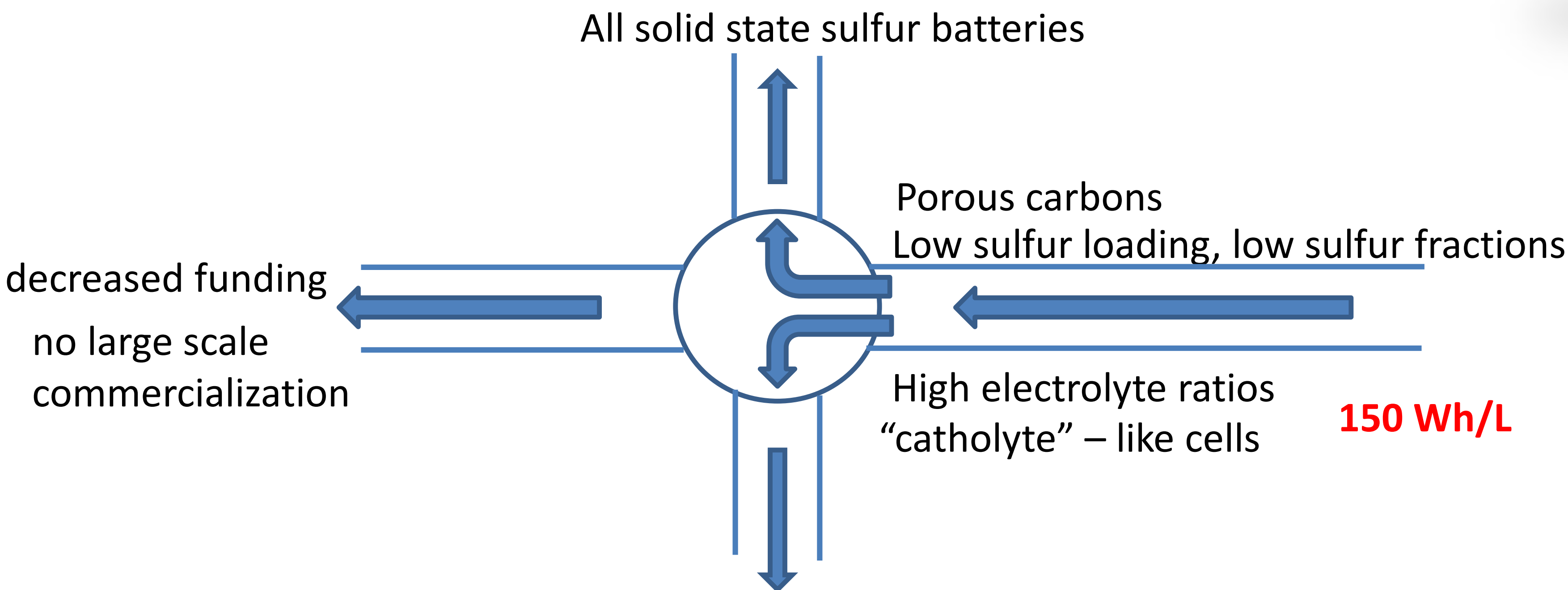
cheese milk cheese

theoretical capacity 1675 mAh/g @ 2V

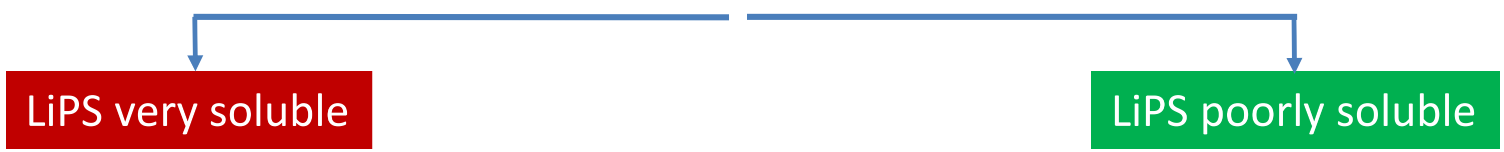
500 - 1000 mAh/g today

Desirable shuttles

The Crossroads



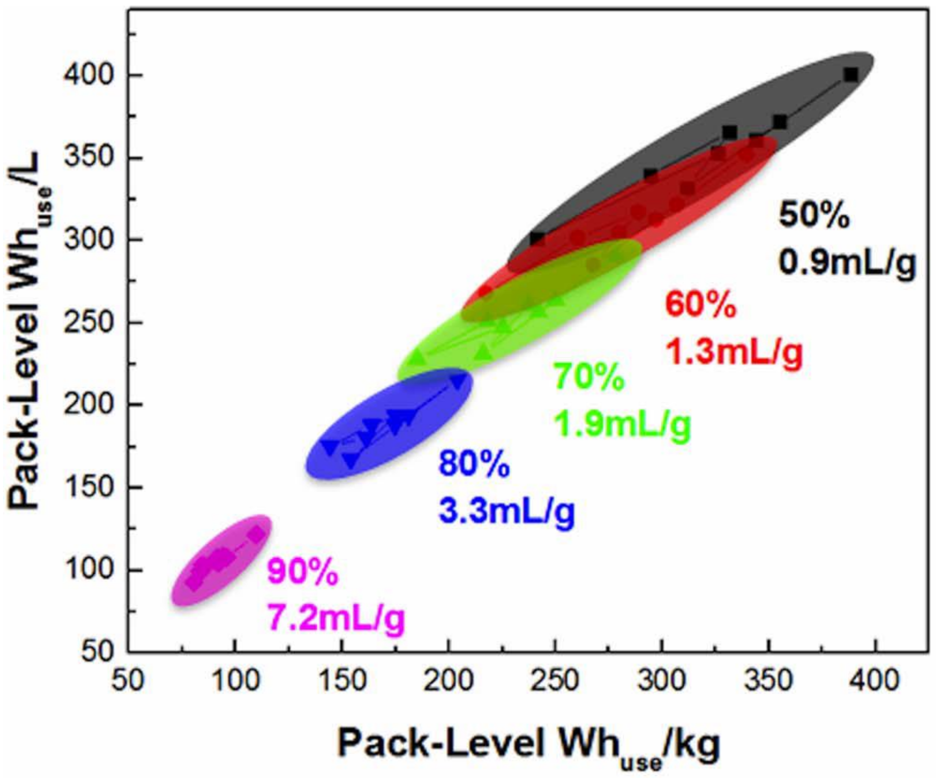
solve the problems with multipronged approaches - find ways for dissolution/precipitation to function in low electrolyte and high sulfur loading



High donor number solvents,
Protected negative electrode – like Li-O_2

“Pb-acid battery”

Li-S for transportation applications: critical metrics



Challenges:

high current densities (~7 mA/cm^2)
high sulfur loading ~ 7 mg/cm^2
electrolyte ~1.3 – 1.9 µl/mg

---- Kevin G. Gallagher *et al*

Calculated cell-level energy density and specific energy for a 100 kWh_{use}, 80 kW and 360 V Li-S battery as a function of the electrolyte vol% in the cathode (50–90%) and excess Li amount in the anode (50–400%).

Gallagher et al., J. Electrochem. Soc., **162** (6) A982-A990 (2015)

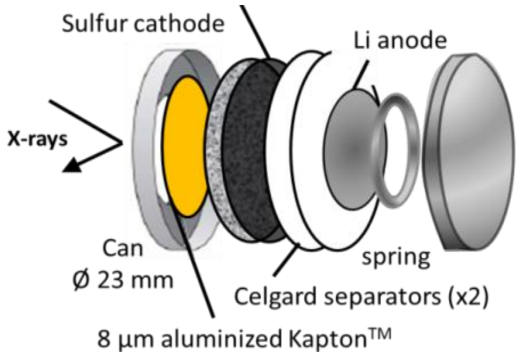
Are these goals achievable - how?

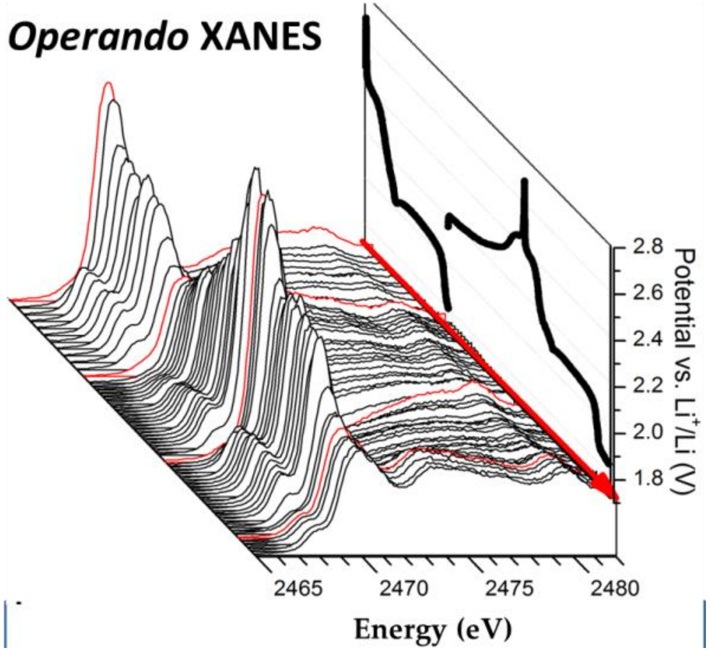
➔ The Problem with Porous Carbon

☑ Good interaction with sulfur

⊗ ⊗ ⊗ No interaction with intermediate lithium polysulfides OR Li_2S

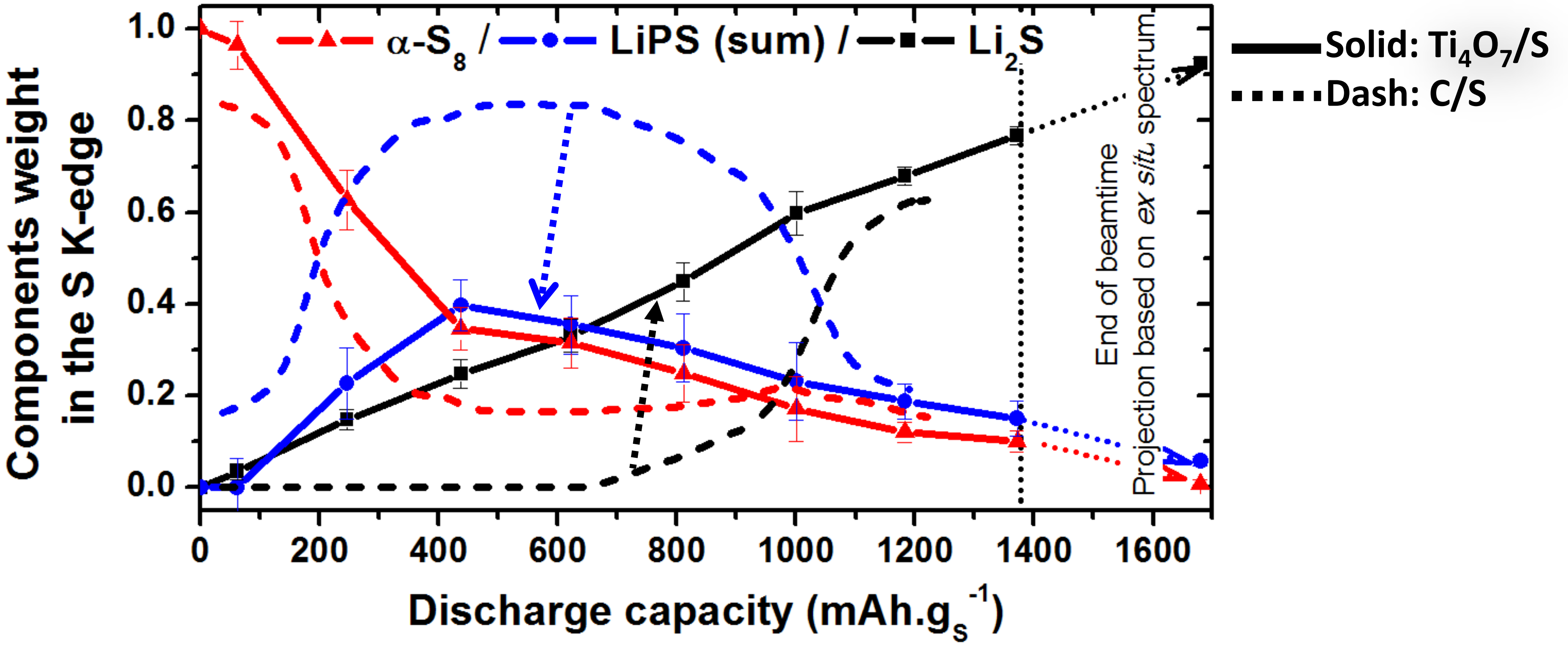
In situ cell: synchrotron (APS)





Cuisinier, Balasubramanian, Nazar, *J. Phys. Chem Lett* (2014)

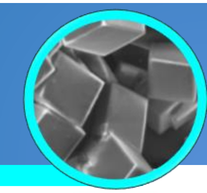
Operando XANES: Ti_4O_7/S cathode shows strong interaction

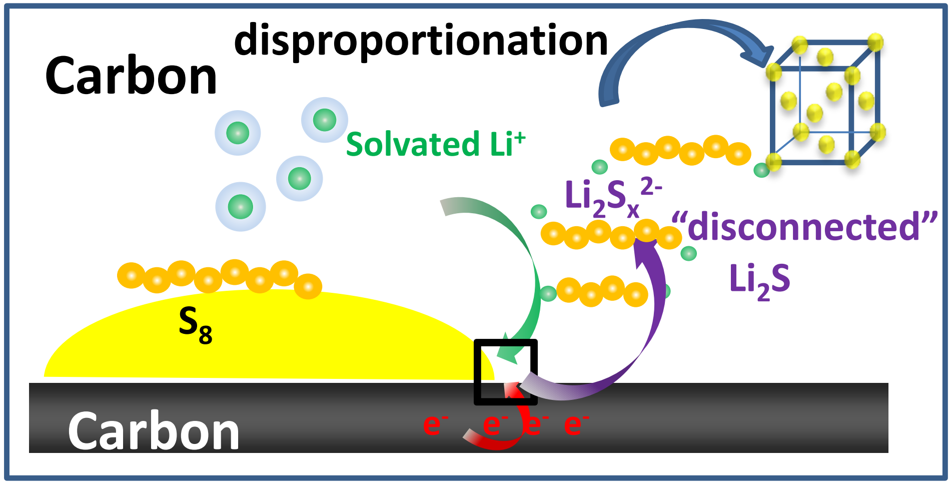


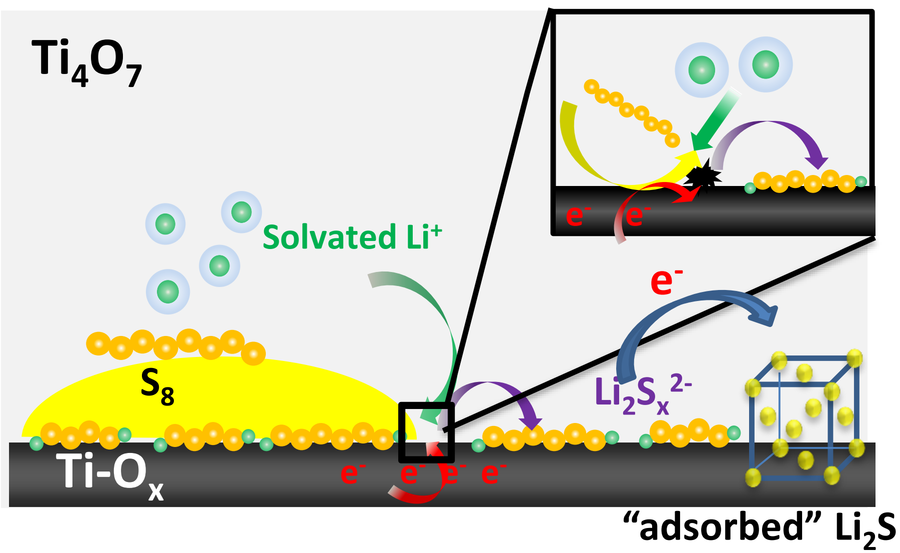
- During discharge:
  - ✓ Much lower fraction of polysulfides at all stages (efficient trapping)
  - ✓ Li_2S precipitates earlier and more progressively

- **Ti_4O_7-polysulfide interaction promotes charge transfer**

Ti_4O_7 - surface enhanced electrochemistry







Upon electrochemical reduction (receiving e^- and Li^+):

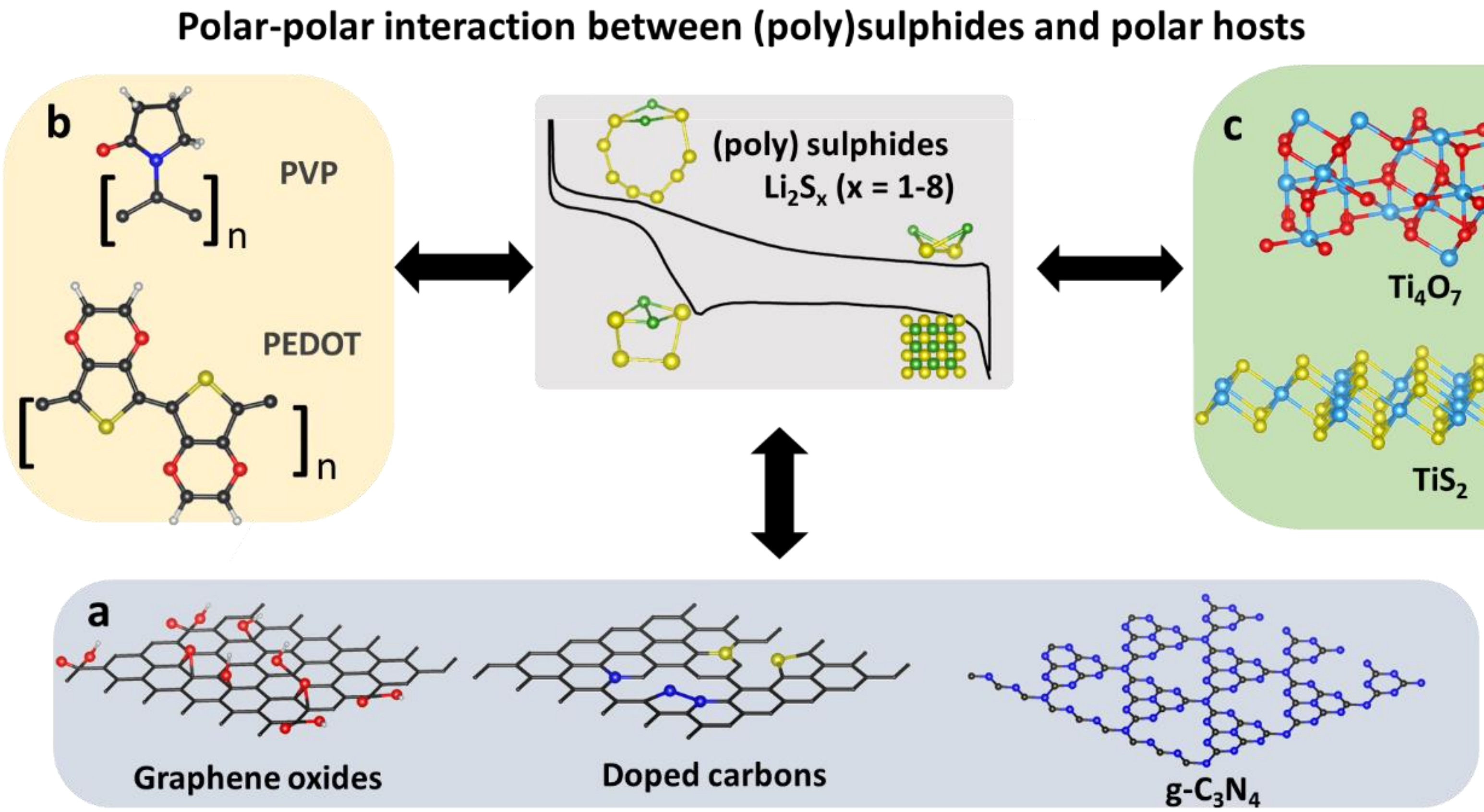
Sulfur reduced and dissolves to form solvated lithium polysulfides
→ Li_2S isolated from electron wiring

Sulfur reduces and adsorbs on metallic oxide surface → "adsorbed" Li_2S

- Uniform deposition of Li_2S
- Suppress polysulfide diffusion/shuttle
- Improved capacity retention

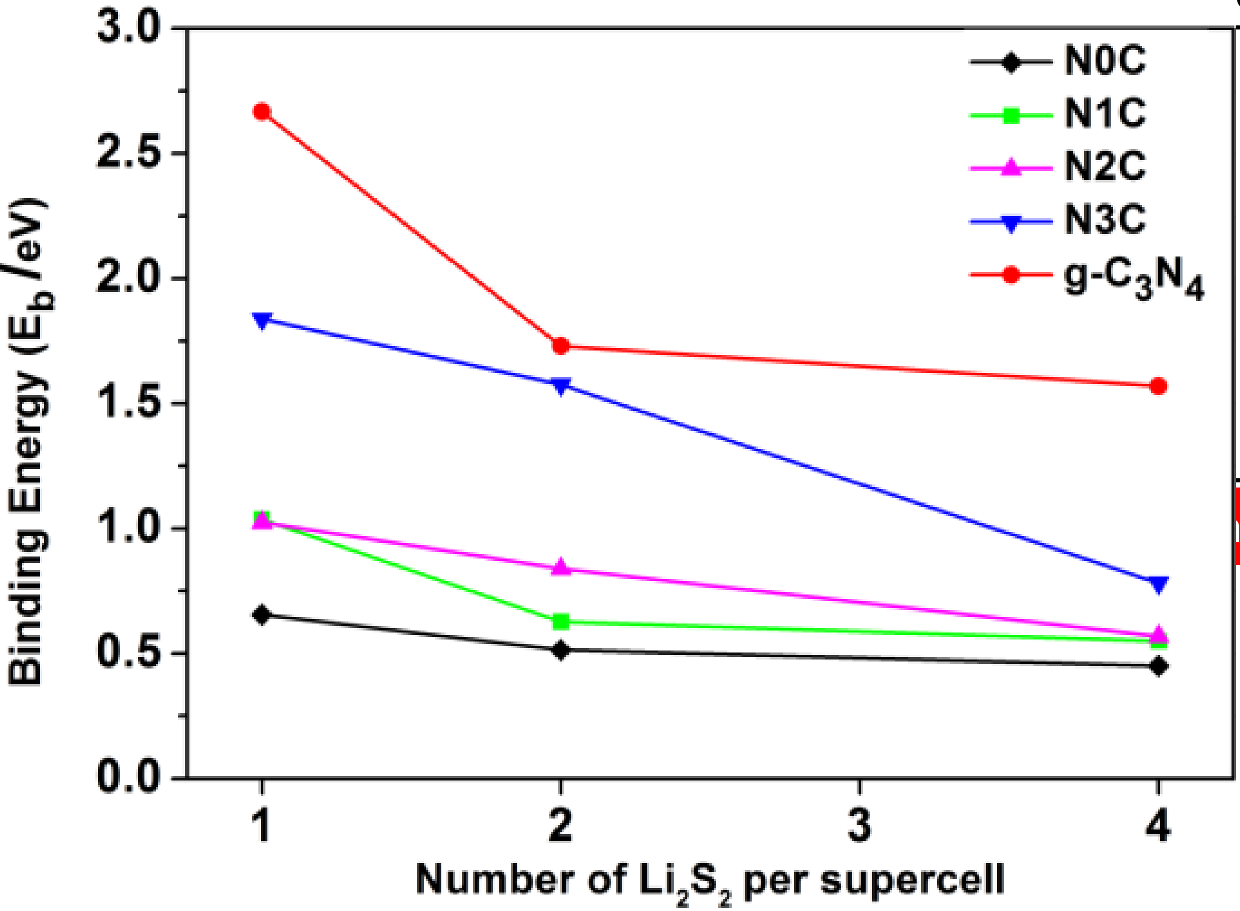
Q. Pang, D. Kundu, M. Cuisinier, L. F. Nazar, *Nature Comm*, 5 : 4759 (2014)

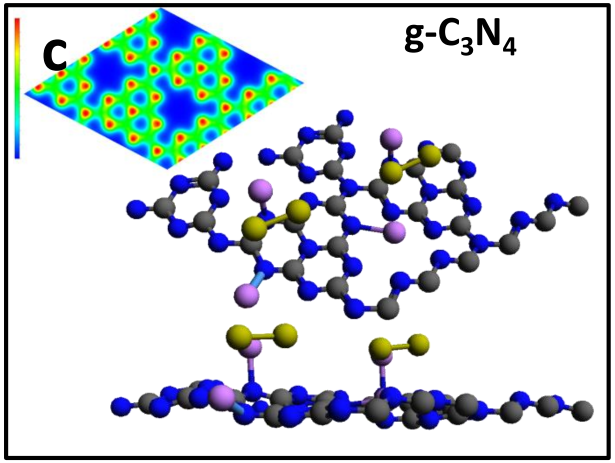
Surface interactions of LiPS with polar hosts are key



First-principle calculations – quantitative study of interactions

- DFT (VASP code)
- Simulated the adsorption of various numbers (1,2,4) of ***Li_2S_2*** molecules
- The substrates span the ***same* basal area**
  - …ed on the substrates



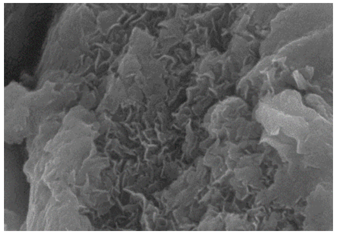


a Li-N bond

14.9 mg/cm^2 sulfur loading
electrolyte/sulfur ratio = 3.5: 1 μl/mg

Pang, Nazar et al ACS Nano, (2016); *Adv. Energ. Mater*. (2016)

Polysulfide chemical trapping: surface-active mediators

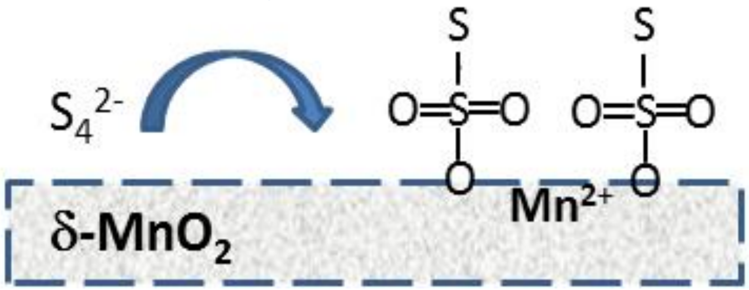


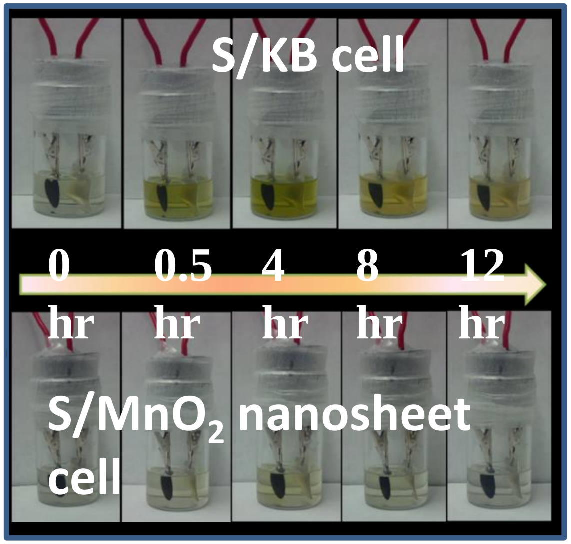
MnO_2 nanosheets – 10 nm thick

75 wt % sulfur/ "inorganic graphene"

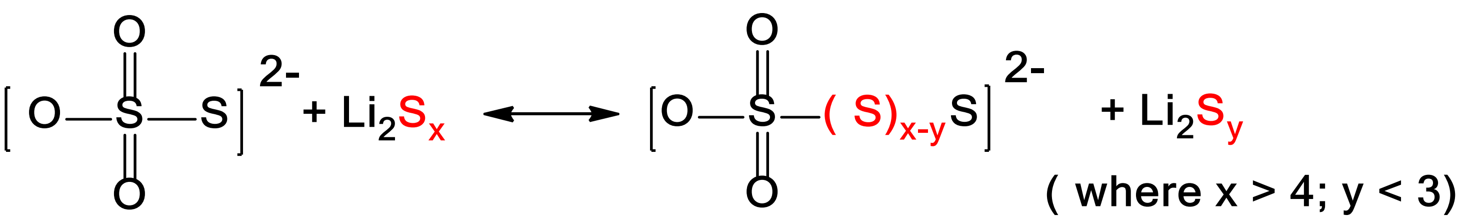
Capacity fade rate = 0.04% per cycle over 2000 cycles

A. Formation of thiosulfate via oxidation of LiPS/ reduction of Mn^{4+}:



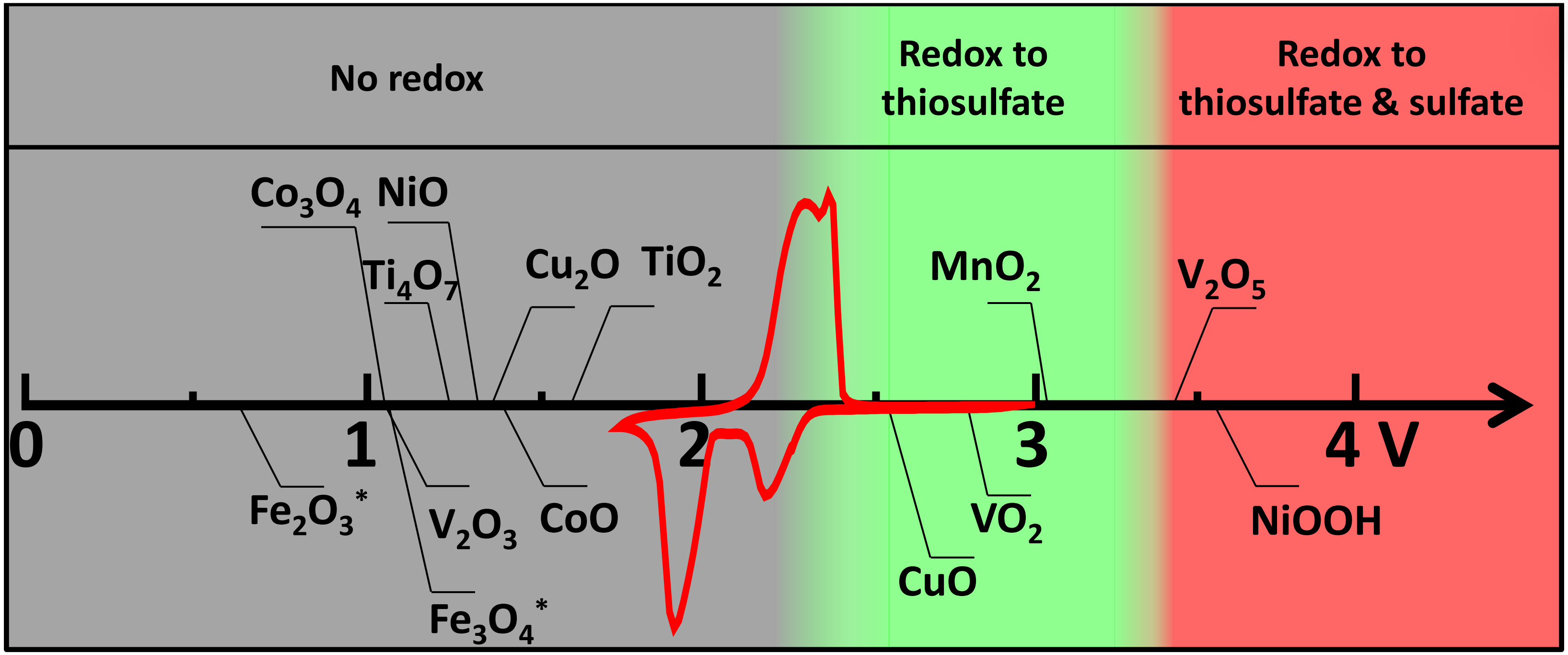


B. Catenation of sulfur to form polythionate complex



Liang, Nazar *et al.*, *Nat. Commun*. 6, 5682 (2015)

The “Goldilocks” Principle

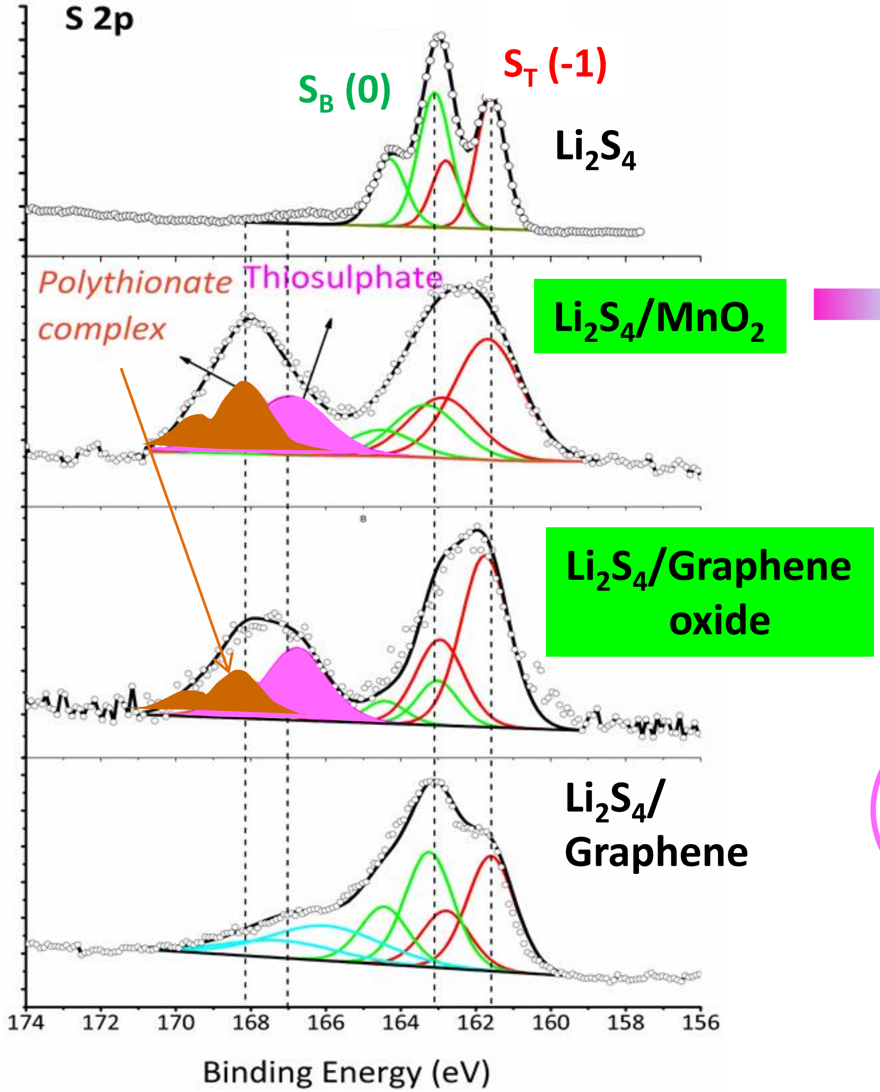


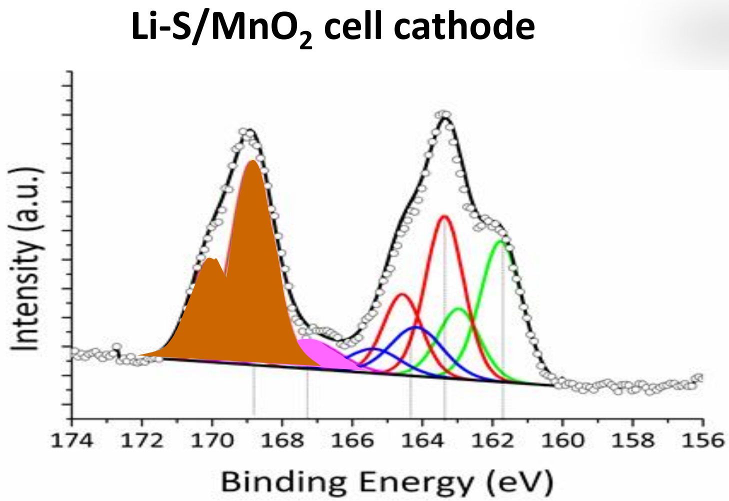
Electrochemical reactivity of different metal oxides with LiPSs as a function of redox potential vs Li/Li^+

Same process occurs for graphene oxide (reduced by LiPS – thiosulfate/ polythionate)

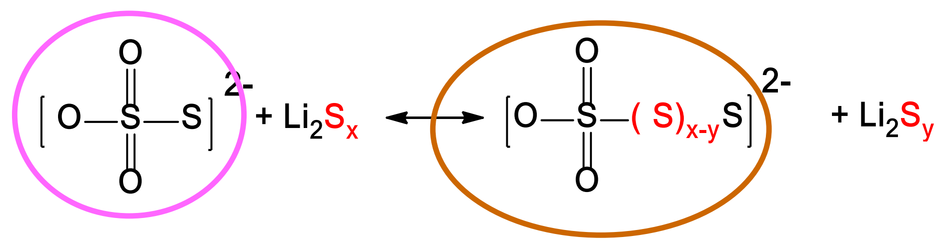
Nazar, Sommers et al., *Adv. Energy Mater*. 6, 1501636 (2015)

Interaction between polysulfide and MnO_2 or graphene oxide



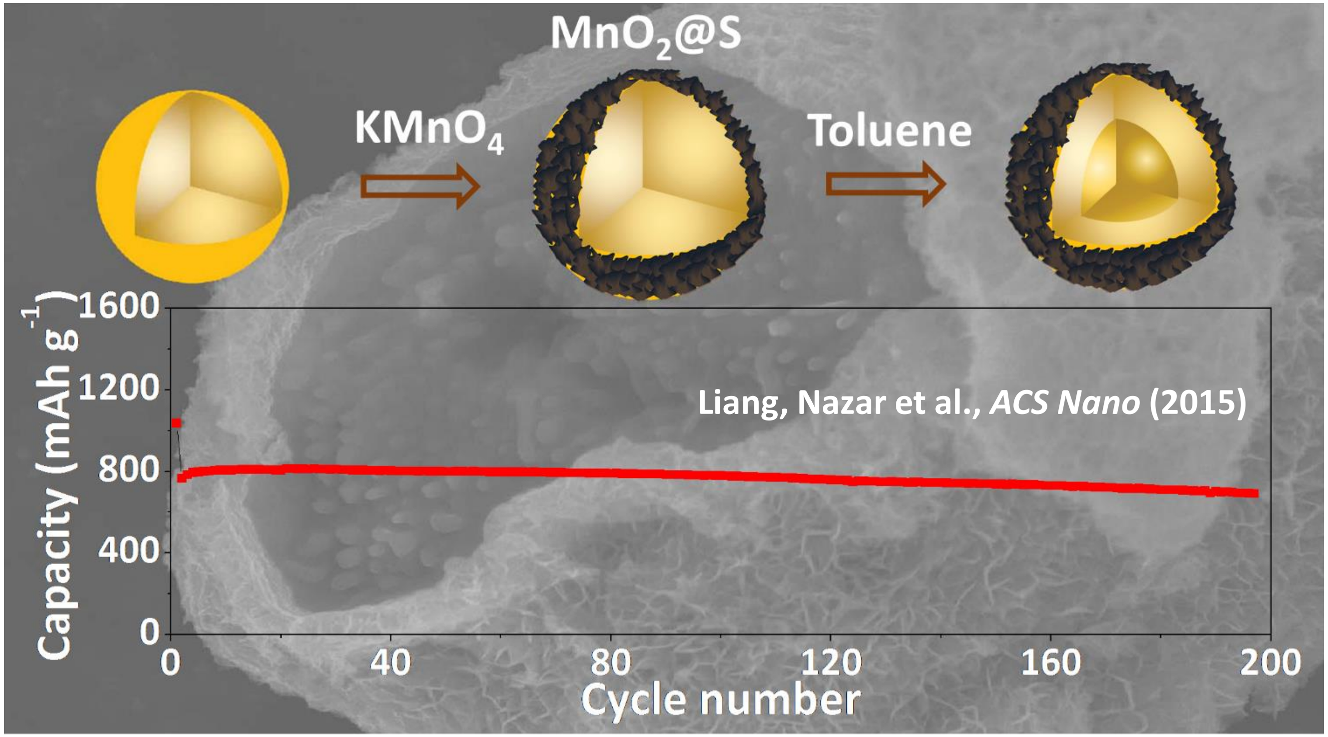


At 2.3 V: partial reduction or oxidation



Core-shell micron-sized sulfur with an inorganic coating

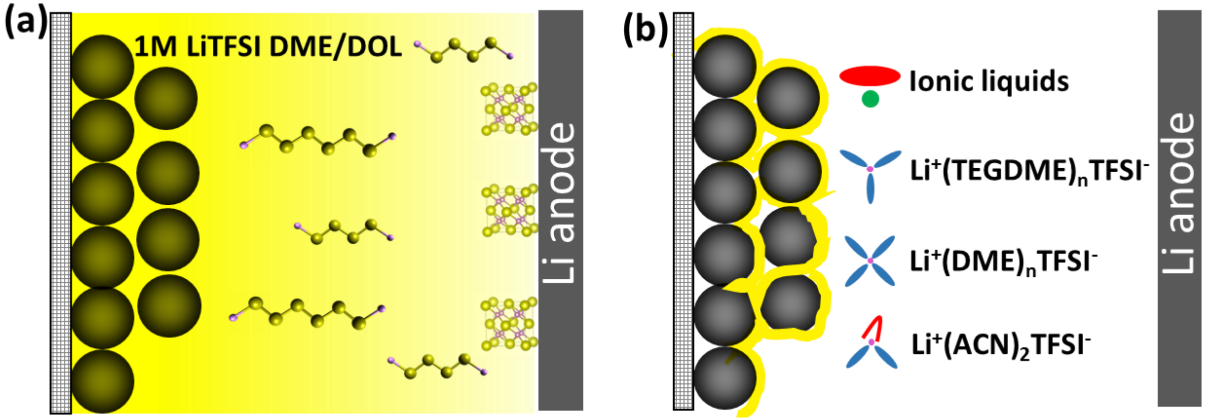
$$6\,MnO_4^- + 3S + H_2O \rightarrow 6\,MnO_2 + SO_4^{2-} + [H(SO_4)_2]^{3-} + OH^-$$

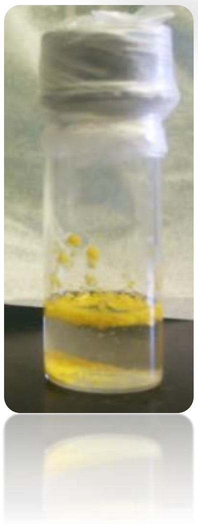


Sustain high sulfur areal loadings

X. Liang, L. F. Nazar *et al, Angewandte Chemie 2015; Adv. Mater*., 2016 on-line

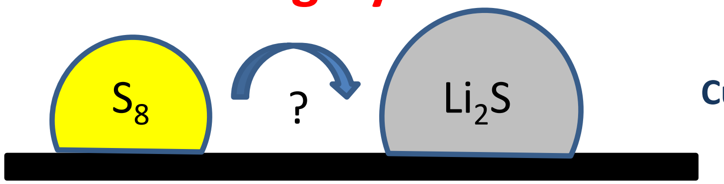
Concept of "sparingly soluble-solvents" for polysulfides





Utilize a "non-solvent" electrolyte

Solid-solid transformation? Highly limited solution process?



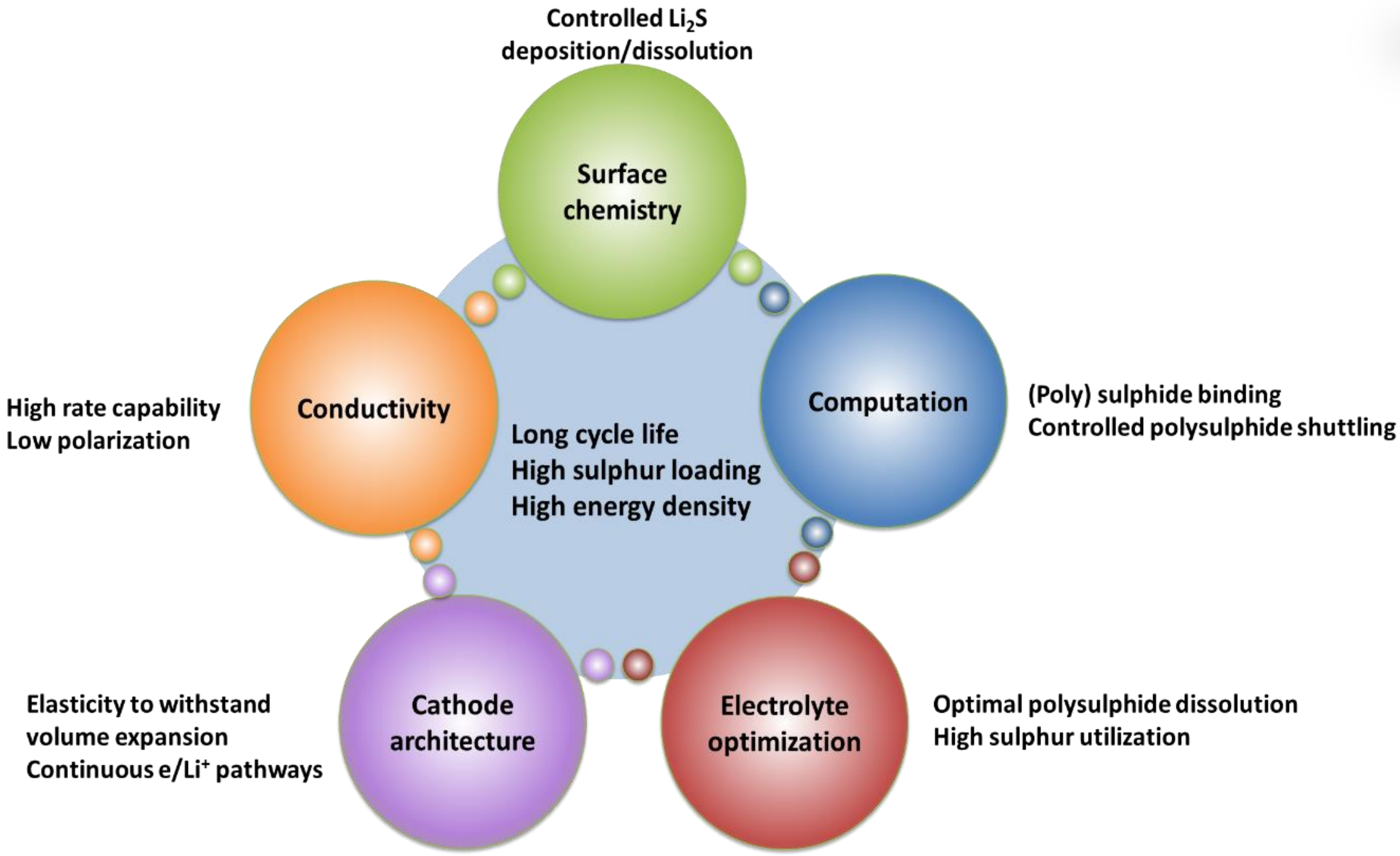
Cuisinier, Nazar et al., EES 2015.

Utilize a sparingly soluble electrolyte

Optimum properties for solution-based reactivity?

Controlling precip^tn of Li_2S – needs a polar metallic host, RMs

Critical Factors for Liquid Electrolyte Cell design



Q. Pang, X. Liang, L.F. Nazar, *Nature Energy (in press, 2016)*

Divalent batteries: intercalation of Mg^{2+}, Zn^{2+} ions

Electron transfer/ion mass not higher than Li^{+}/e^{-}

but…

✓ **Advantage: metal anode (no dendrite formation, i.e., Mg)**

- greatly increases energy density compared to carbon in Li-ion cell

Chevrel phases (Mo_6S_8) first to be studied as cathode*

Mg insertion examined in oxides**

❖ **Disadvantage: multivalent cations exhibit (?) low mobility in most high voltage host materials (ie, oxides)**

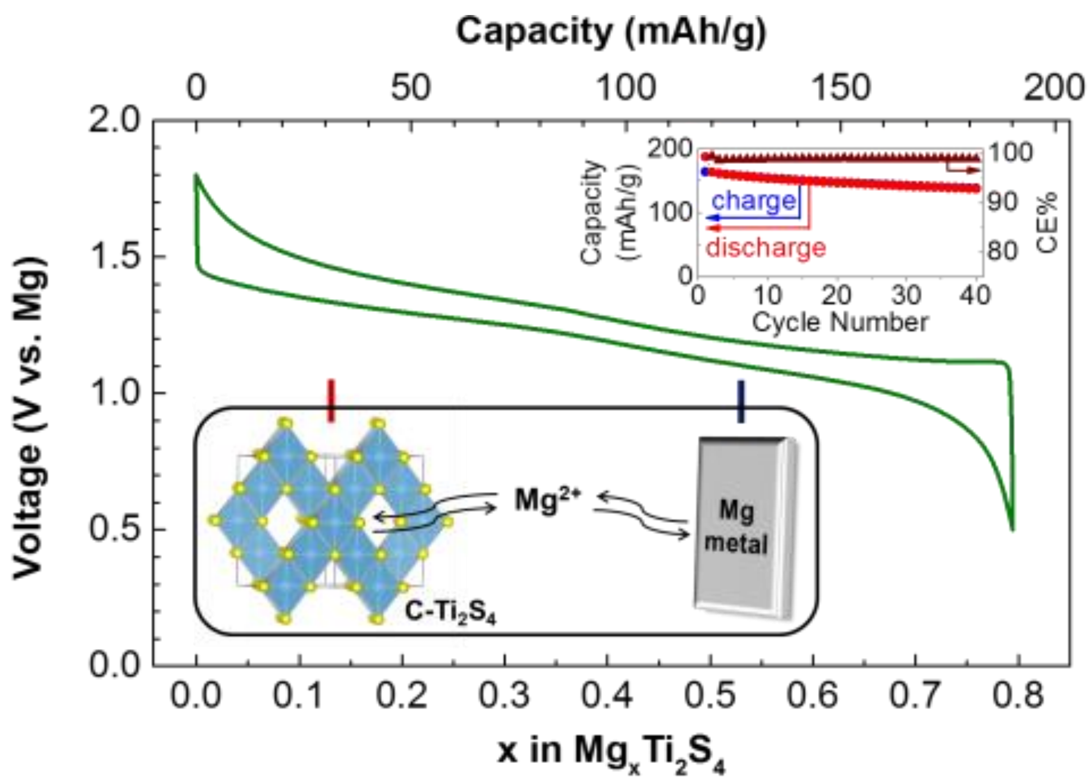
- desolvation penalty for multivalent cations high

- nascent understanding of factors at play

D. Aurbach et al., *Nature 2000
**** P. Novak *et al*, 1997**

"Soft" anions: Mg (de)intercalation in the thiospinel Ti_2S_4

Mg full cell with thiospinel cathode shows 190 mAh g^{-1} capacity, twice that of benchmark (2000), and relatively stable capacity retention.

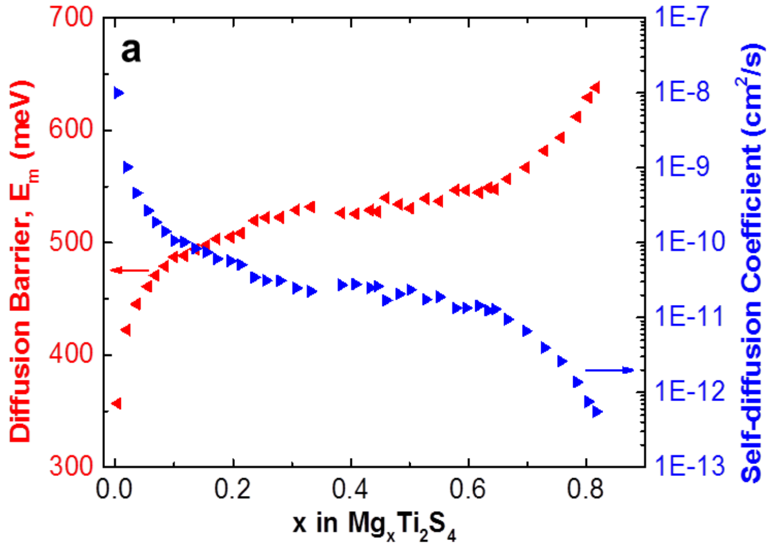


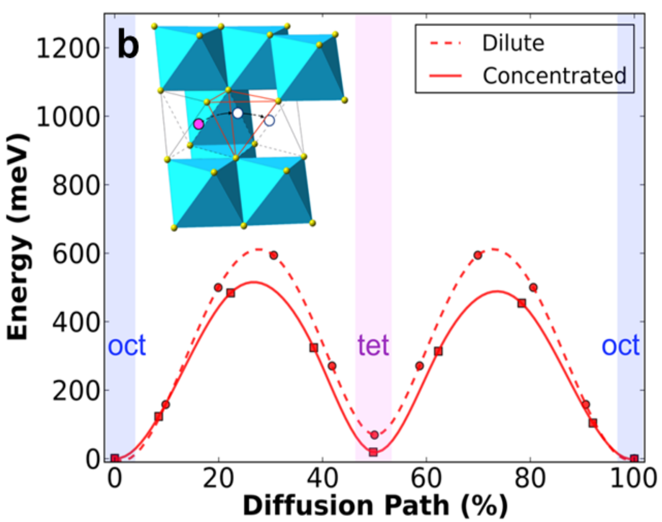
X. Sun, Z. Rong, G. Ceder, L.F. Nazar et al., *Energy Environ Sci (2016); ACS Energy Lett 2016*

Diffusion energy barriers in Ti_2S_4 agree with computation

In collaboration with Berkeley Theory Team: M. Liu, Z. Rong, K. Persson, G. Ceder

Mg self-diffusion coefficients (60° C) and corresponding energy barriers for Mg diffusion in cubic Ti_2S_4 calculated in dilute and concentrated limits





D_{Mg} (at 333K) expt: 530 meV; theory: 550 meV

D_{Mg} (at 333K) ≈ 0.1X D_{Li} at 298 K

Nanomaterials required

A.C. James and J.B. Goodenough, Solid State Ionics, **27**, 37 (1988).

Multivalent Intercalation (Aqueous)
Advantages

- Divalent cation does not require desolvation from solvent shell
- Screening of divalent cation charge in lattice by solvent – enhanced mobility

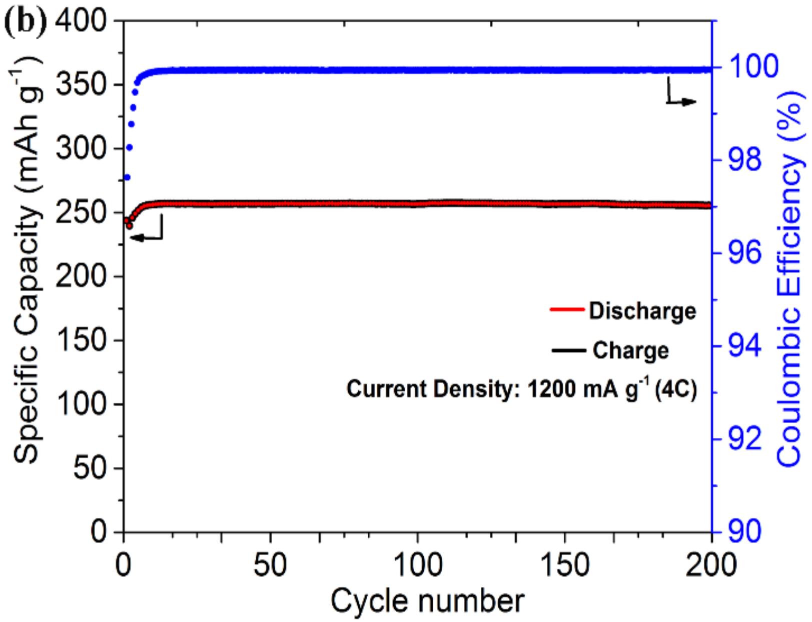
2016 to be a breakout year for stationary energy storage

01/05/2016 - Philippe Bourchard

Aqueous Zn-ion batteries

Why Zn metal ?

- Stable in water: high corrosion resistance
- High abundance, production; non toxic
- Suitable redox potential (0.76 V vs. SHE) High volumetric energy density (d: 7.14 g cm^{-3})
- Small exchange current for HER on Zn: large kinetic voltage window ~2.4 V for Zn based aqueous rechargeable batteries.



Aqueous Batteries ?

- Low-cost, safe, easy to manufacture and dispose

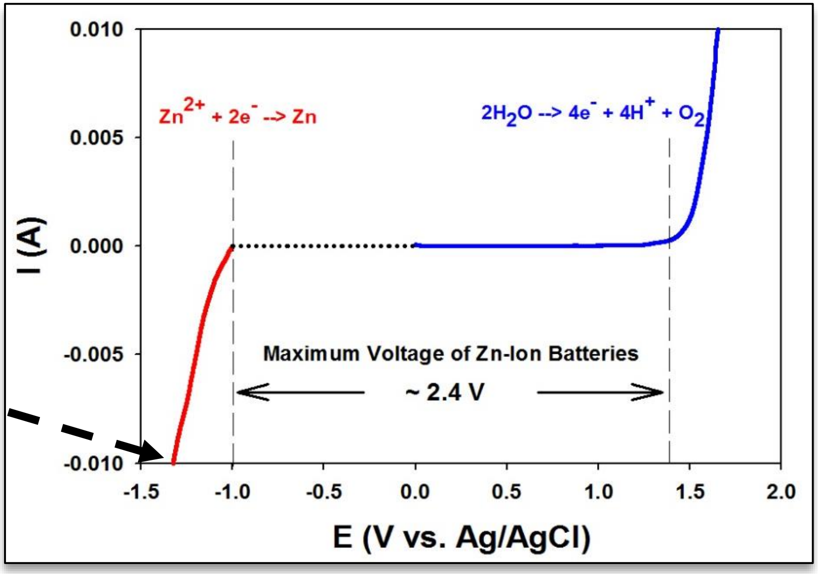
Aqueous Zn-ion Batteries >> Safe and environmentally benign alternatives to their aprotic counterparts, can have ultra-high rate capabilities.

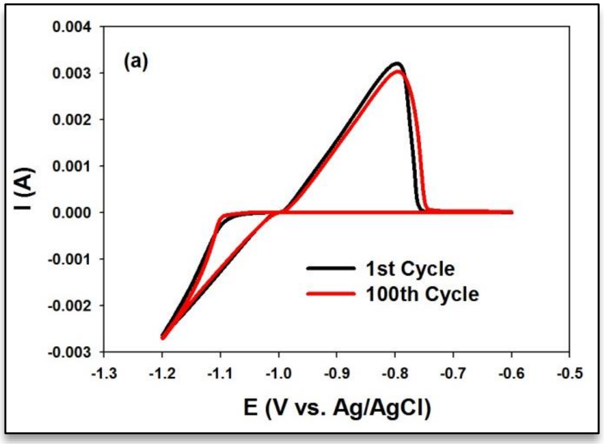
Efficient Zn stripping and plating

Highly reversible Zn stripping and deposition

WE: SS rod
CE: Zn disk/metal
Electrolyte: 1M $ZnSO_4$-H_2O

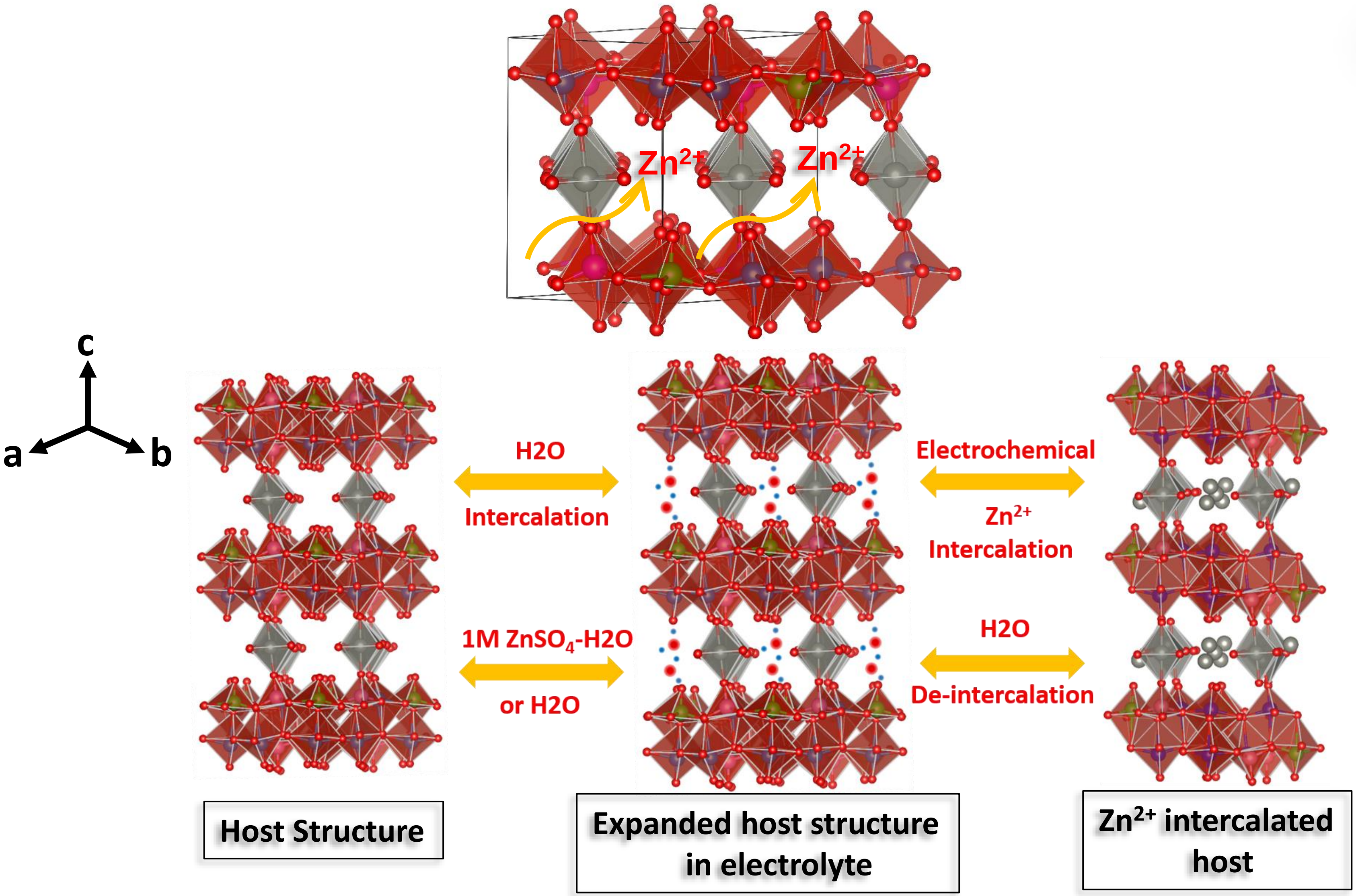
HER
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$





- **$Zn^{2+} + 2e^- \leftrightarrow Zn$ with ~100 % coulombic efficiency (Qox/Qred)**
- **Rechargeable aqueous Zn-ion batteries: ~2.4 V window**
- **No dendritic growth at pH < 7**

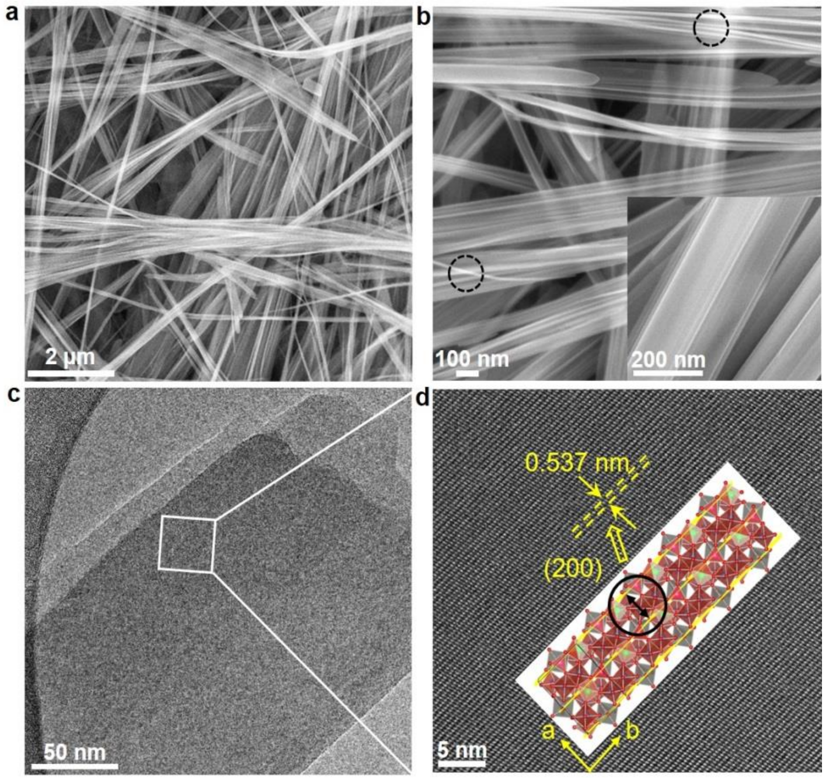
Layered Host: Water Assisted Facile Zn^{2+} Intercalation




VIENNA

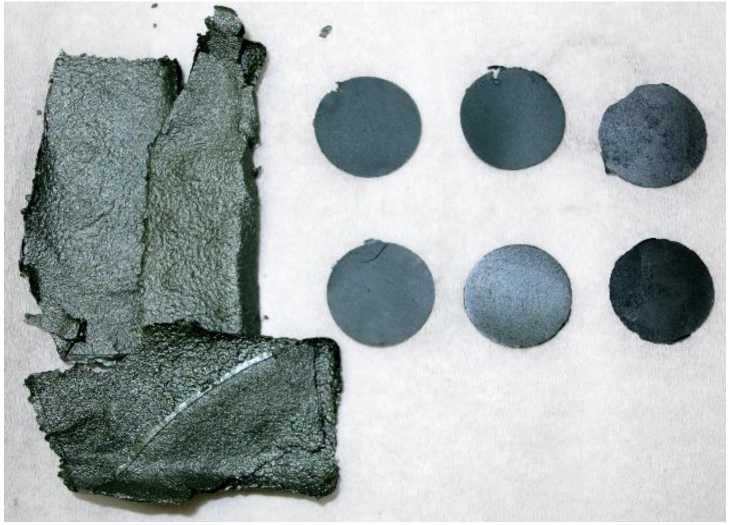
Nanofiber morphology - short diffusion path, easy fab

SEM/TEM images of nanofibers

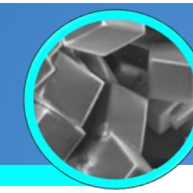


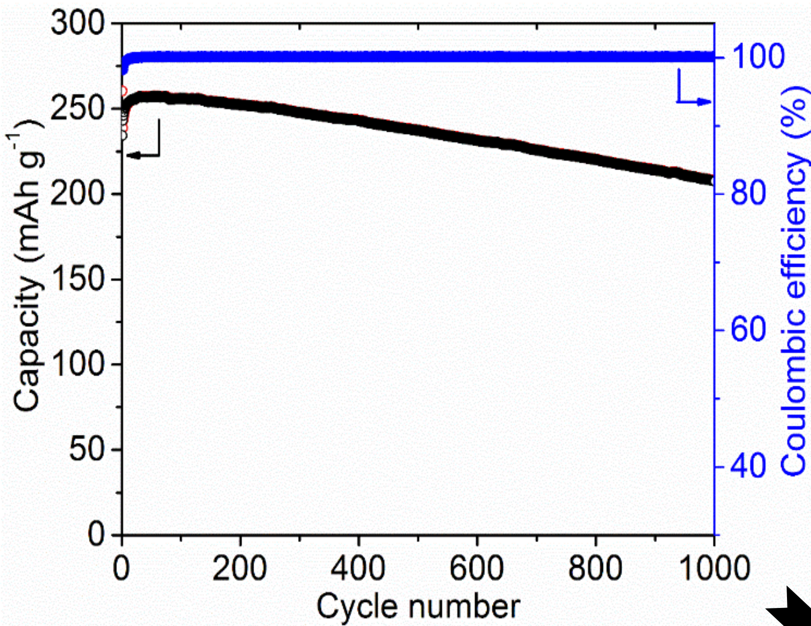
Free-standing electrodes

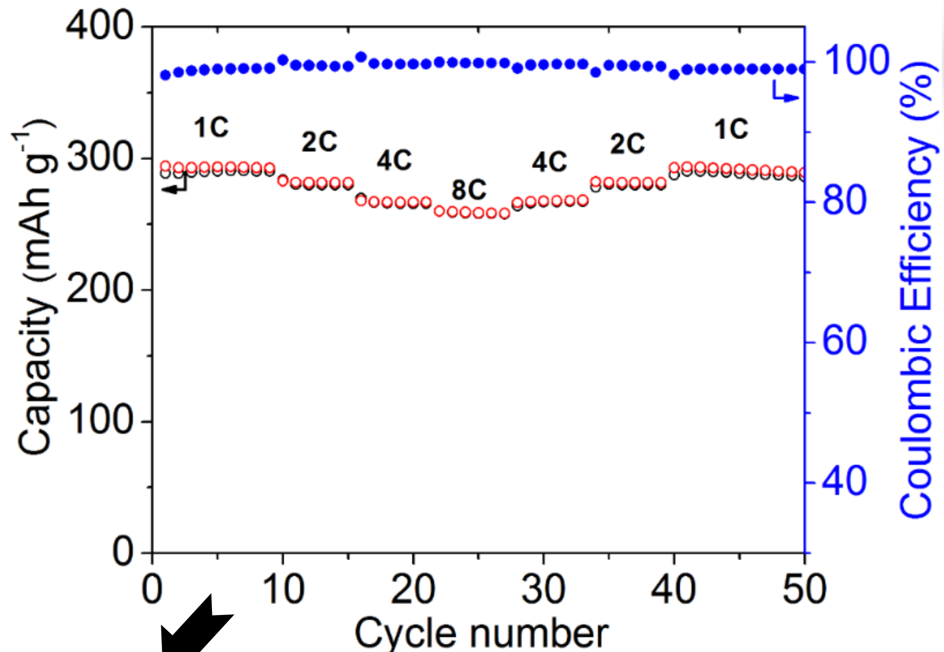
H_2O-slurry
H_2O-based binder



Sustainable & High-Rate Zn^{2+} ion Storage





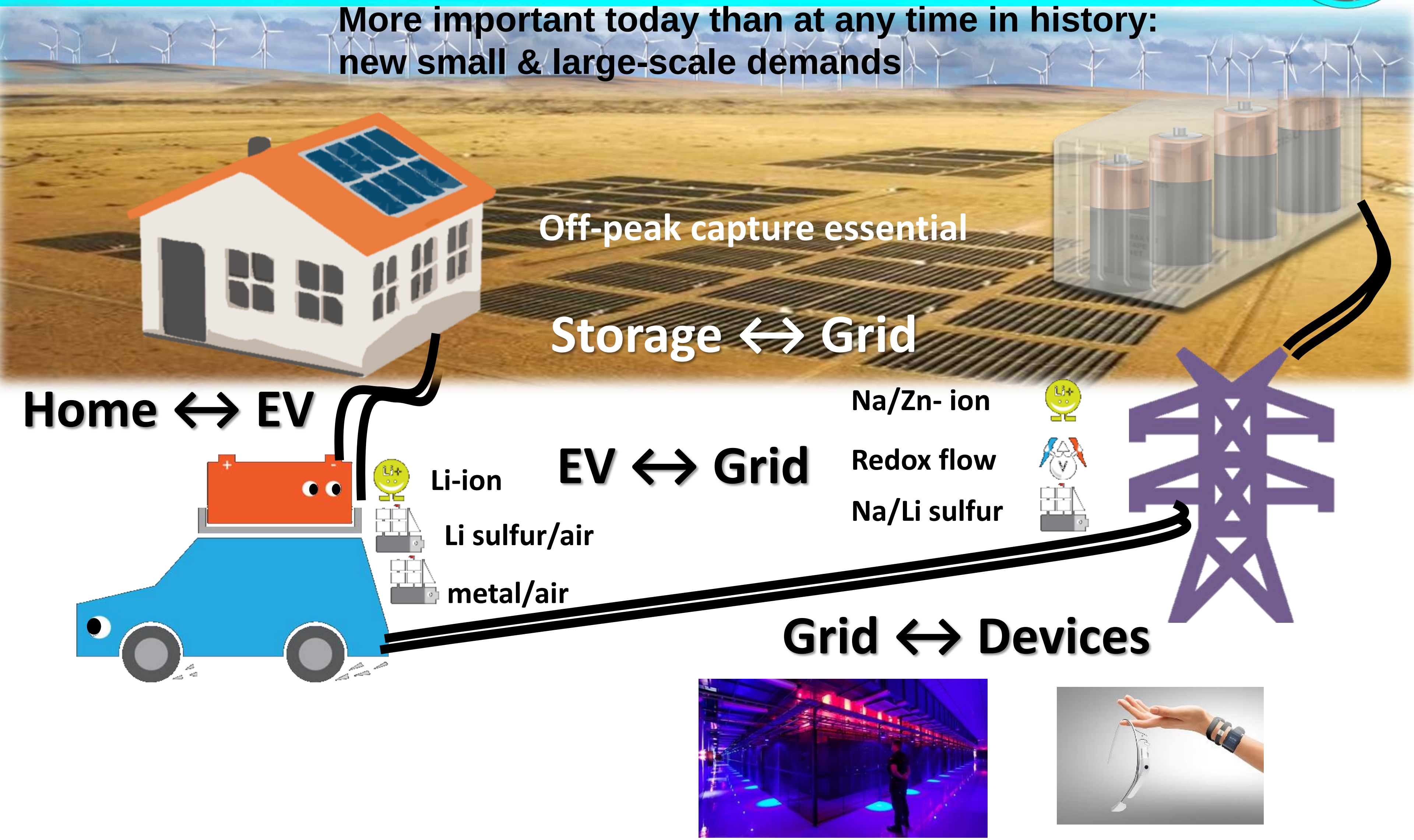


- **Highly reversible Zn intercalation & stable cycling**
- **1000 cycles: ≥ 80 % capacity retention**
- **Energy density (pouch cell): 450 Wh/L**
- **Coulombic efficiency: ≥ 99%**
- **High rate capability: discharge/charge in 8 min**

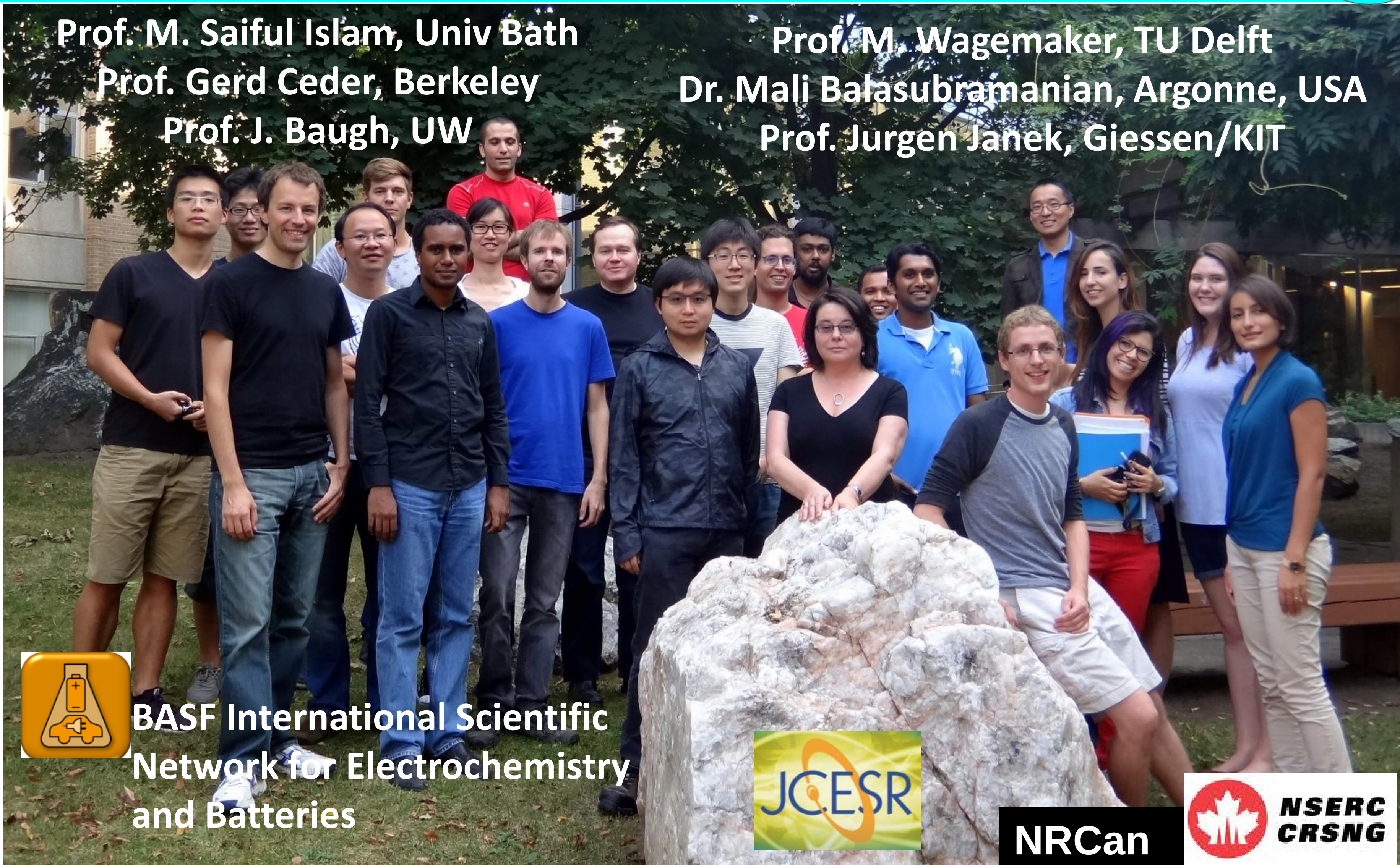
< $70/kWh

D. Kundu, B. Adams, V. Duffort, L.F. Nazar, *Nature Energy* (2016)

Integrated electrochemical energy storage



Research team and collaborators



Thank you – we welcome visitors

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